RESEARCHES ON CELLULOSE

III

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BY

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PREFACE

FOR reasons stated in the text the plan of the present volume, No. III. of the series, is modified from that of the preceding. It is presented rather as a personal and impressionist view of progress in research in the field of 'Cellulose' for the period 1905-10. The preparation of the work has been delayed to include research work published in 1911.

In regard to the future, and the progress of research, it is clear to us that no chemist can approach the subject of 'Cellulose' in any comprehensive way without meeting with problems belonging to general philosophy.

On this broad platform of thought no writer, who claims to be a student, will presume to have any special insight: the reader, according to temperament, will either elect to live with such problems or accept the 'contracting out' attitude of those who find the fascination of investigation and discovery exclusively sufficient for the intellectual day.

We have ventured to deal with one or two questions of this order, which appear to be inevitable in the sense that they are invariably presented to young students in the formal textbooks of the science.

And it is only to the young student that we address ourselves in enjoining the duty of clear thinking, should he be

interested in pursuing problems which belong to the general perspective of the science.

As to progress in the special sense, and any probable contribution resulting from research in the field of cellulose, we cannot ourselves avoid very positive anticipations of a much deeper knowledge of matter, as matter, to follow from the application of physical methods to the investigation of cellulose, its derivatives, and its analogues of the group of colloidal carbohydrates.

To this end we hope the present notes from one of the active centres of research may contribute.

We have to acknowledge the assistance of Mr. W. N. Bacon, B.Sc., in the correction of the proofs and the preparation of the index.

CONTENTS

BIBLIOGRAPHY

We particularly call attention to the following works :—

F. CZAPEK. BIOCHEMIE DER PFLANZEN. Jena, 1905.
An exhaustive treatise on plant physiology.

C. G. SCHWALBE. DIE CHEMIE DER CELLULOSE.
Berlin, 1911.
A very full account of cellulose chemistry, with a corresponding bibliography.

E. ABDERHALDEN. BIOCHEMISCHES HANDLEXIKON.
Berlin, 1911.
Vol. II. contains a very full and exhaustive account of the general chemistry of cellulose, and compound celluloses, as of the "cellulosines," and the several groups of carbohydrates.

Wo. OSTWALD. GRUNDRISS DER KOLLOIDCHEMIE.
Dresden, 1909.
This is one of the many volumes now appearing in Germany on the general problems presented by the colloidal state. This particular volume is a general account of colloidal matter, and has been mentioned in the text, on page 9.

E. C. WORDEN.   NITROCELLULOSE INDUSTRY.   London, 1911.

This is a technical and technological work, dealing not only with nitrocellulose, but with cellulose derivatives generally, including acetate and viscose.

BERICHTE DES VEREINS DER ZELLSTOFF UND PAPIER CHEMIKER.   (S. FERENCZI, Berlin.)

Contains important original work on scientific and technical problems.   .

C. F. CROSS.   TWO LECTURES ON CELLULOSE, Institute of Chemistry.   Jan.-Feb.   1912.   (Inst. Chemistry, London.)
                                                              .
Deals with 'cellulose' in relation to the career of chemist.

CELLULOSE III

CHAPTER I

INTRODUCTION

In dealing with the contributions of researches in the domain of Cellulose Chemistry for the period 1905 to 1910, an element of progress enables us to change our working plan from that of our previous works.

This progress results from specialisation at more than one centre of work; O. N. Witt in Berlin, H. Ost in Hannover, C. G. Schwalbe in Darmstadt, and E. Knoevenagel in Heidelberg, amongst others, have inspired important investigations, sufficiently important that is, to identify the institutions which they represent with the main stream of progressive investigation in this field.

Such investigations involve as a basis a critical study, and in their final form of publication, an exposé of all current literature of the subject; we are to this extent relieved of the self-imposed task of passing this same literature in critical review. Schwalbe has been active in a wider field than that of special and sectional research, and has produced a comprehensive general treatise on 'Cellulose' in two volumes, of which the critical bibliographical foundation is so thorough and exhaustive as to further relieve us from maintaining a position as chroniclers of progress, measured in terms of the records of the standard journals of research.

But also new technical institutions have come into being devoted to the interests of 'Cellulose'.

In this country we have recently (1910) founded a Textile Institute which, though not exclusively devoted to cellulose textiles, is mainly concerned with this section of our most important group of industries.

This institute is already a centre of publication and of influence in promoting investigations. A first objective is evident in a scheme of research attacking the problem of the relationships of spinning quality of cotton to actual composition (p. 126).

In Germany an important and flourishing society of recent formation (1905) is the ' Verein der Papier & Zellstoff Chemiker,' a centre of publishing activity, and a society which *stimulates* research by formulating problems requiring solution, and encourages the workers by a scheme of prizes.

But beyond this direct promotion of research work in the field of cellulose chemistry and technology, this society publishes an annual technological record, a 'Jahresbericht,' which is not a mere record but an abstract account of published research work, including patents. It would obviously be a labour of redundancy to duplicate these records.

There is another important influence which is more prominently operative with the growing importance of new cellulose industries : that is, the work of patent revision in connection with the grant of patents, more particularly by the German and United States Patent Offices. Opposition to the grant of patents, or attack of patents already granted, involves 'expert' criticism of a high order, and the procedure in such cases is based largely on 'Gutachten,' or reports, the preparation of which not only involves close critical study of the subject-matter of invention in relation to antecedent history of an art or process, but experimental investigation of purely scientific order. The scientific results of such work are for a time immured in the records of the patent offices, but are ultimately put on open record in the journals of the science. It must also be noted that the new cellulose in-

dustries based upon chemical treatment of cellulose have created centres of technical and scientific work incidental to the control of industrial operations, and with a further view to progressive evolution of the industry.   The records of such centres have a longer period of 'live-burial' and for obvious reasons ; of actual publication from these centres we have so far only patent specifications, but there is promise of publication of scientific investigations of general import, which engage the chemical staff of these manufacturing corporations.

This reservation of results of investigation is equally characteristic of the older special cellulose industries.

In connection with celluloid or xylonite and the explosives industries, a very large amount of research work is put through, but 'shelved' so far as science is concerned.

We except the special publications of the Neu-Babelsberg 'Centralstelle,' which are important sectional contributions. Some of these have been noted in our previous works as contributions of scientific method as well as of industrial developments.

From this brief survey it is evident that specialisation in this field proceeds apace, and that the specialisation is mainly that of technology.

It may not be superfluous to enumerate the main sections of a classification of cellulose industries, which gives an impression of the area comprehended.

APPLIED CHEMISTRY OF CELLULOSE AND DERIVATIVES.

Cellulose textiles.	Raw materials in relation to spinning quality; bleaching, dyeing, finishing of manufactured textiles.
Papermaking.	Raw materials ; boiling, bleaching, and preparation ; physical and chemical properties of papers in relation to uses.
Cellulose as constituent of agricultural produce.	Food stuffs, etc. : animal digestion of celluloses and compound celluloses.

Cellulose derivatives :—

Organic solvents.			Aqueous solutions.
Nitrates.	Acetates.	Formates.	Cuprammonium, Viscose.
Celluloid,	Celluloid	Celluloid	Artificial fibres, films,
artificial	substitute,	substitute,	agglomerates.
silk, ex-	artificial	artificial	
plosives	fabrics.	fabrics.	

But from the point of view of pure science this technical specialisation has only a subordinate interest. The position of cellulose in relation to chemical science as a whole appears to be comprehended in its general identity as a carbohydrate. It will perhaps be admitted that this important and fundamental fact has had rather the effect of paralysing research. A long · series of textbook paragraphs, and encyclopædic articles descriptive of cellulose as a chemical individual, may be taken as illustrating the effect of such paralysis or mental polarisation under the influence of a dominant fact or idea.

There is also the psychological influence of the evolutionary history of chemical science. Passing through such phases of realised conceptions as of the stoichio-metrical equivalents, atom, molecule, valency, equivalent function, followed by the intensive developments of the truly organic fabric of the science in the region of fatty and aromatic compounds, it is not surprising that the science in following lines of least resistance or of greatest immediate result, has been specially influenced by these very comprehensive generalisations, nor that, according to this order of idea, compounds such as cellulose have been neglected.

The study of cellulose by the investigation of derivative compounds can be compared with travel in an unknown country, whereas the study of compounds in obvious or ascertainable relationship with bodies exactly defined in terms of the general laws of the science, suggests a carefully mapped region, with all the added advantages of railway communication.

It is difficult for a chemist to take a stand outside a section

of the science in active evolution and estimate the proper incidence of any of our theories or generalised conceptions within that section. Thus with cellulose, and we may also say with starch, it has been tacitly assumed that when fully investigated our future exact knowledge of these bodies will take expression in terms of already established theories. There is a suggestion in chemical literature that total synthesis of compounds is equivalent to quantitative knowledge of particular forms of matter. Starch and cellulose presenting many analogies, and starch being quantitatively derived from dextrose, it is assumed that all that remains to be exactly established for each is the actual configuration of a polyanhydride, composed of unit groups of the general type of dextrose.

These colloidal forms of matter have been vaguely held to represent polymerised molecular aggregates of very large, perhaps indefinitely large, molecular dimensions. There are many records of attempts to assign definite magnitudes to starch and starch derivatives by applying methods of measuring co-ordinated physical properties, which give consistent figures in the cases of compounds of simple molecular dimensions; in lesser degrees, by reason of relative difficulty, such methods have been applied to cellulose derivatives. The application of the terminology and conceptions of molecules to these compounds involves the implicit assumption (1) that the colloidal state of matter has no essential feature of differentiation from the crystallised *qua* the form and mode of activity of its ultimate constituent groups (2) that the specialised massforms of organic, in the particular sense of organised matter, have no significance to the chemist : being, that is, superimposed upon, and external to the matter itself.

In regard to (1) it has been assumed that colloidal matter in solution will affect the physical properties of the solvent so that differences of freezing-point, boiling-point, or vapour tension are an exact measure of the molecule of the solute.

It has been evident, moreover, that the assumption has been strained against much direct experimental evidence that the limits of general application of the underlying law or theory had been passed, and the formulæ expressing 'the law' no longer apply.

Thus in the simplest case of observed depressions of freezing-point, those, in the case of typical colloids, are found to bear no proportion to the mass-ratio of solute to solvent.

In regard to (2) we may also have to reckon with psychological factors. It has become a textbook commonplace that the 'Vital Chemistry' of the early part of the nineteenth century has lost all significance in view of the now general synthesis of 'organic' end products. It would appear, moreover, from the textbooks that controversy on or around this point has also lost significance, being swallowed up in the generalised conception of 'Matter' and the unitary conception of the complementary 'force' or energy function which conditions or expresses chemical activity.

We can admit that the facts are clear: but in textbooks of 'organic chemistry,' more especially, the statement of fact is usually clouded by an interpretation which goes beyond or outside the facts.

Thus 'organised' matter has no significance as distinct from 'organic' matter, and the term 'organic' is better substituted by neutral terms indicating the fundamental and exclusive relationship to the element carbon. In the 'interpretation' it is frequently stated that the specialised mass-forms of organised matter are the exact counterpart of the special forms of crystalline matter. This, however, is a departure from fact, and imparts a theoretical dogma, probably the substitution of one superstition by another.

The root idea of crystallography is identical invariability, the root idea of the world of living matter is essential individual variation.

Crystalline form, which is proximate and visible, is ultimately related to the form and motions of constituent atoms and molecules : organised matter in its proximate form is essentially amorphous, in fact the inconceivably high order of plasticity postulated in the materialisation of vital effects implies in vital matter a neutralisation or suppression of motions or stresses of the individual component groups, which otherwise determine crystallisation. Just as photographic reproduction requires a surface whose minute structural details are of inferior dimensions to those of the picture. This characteristic of the colloidal state is common to a diversified range of compounds as they exist in the natural order, and probably a general characteristic of all forms of matter under certain conditions of action of force or super-force. Living matter implies a physical dominating cause operative in and upon a colloidal medium.

The dogma that this force or cause is *ab initio* an intrinsic property of matter, i.e. ultimate matter, appears to rest on a psychological basis : perhaps a certain 'passionate' preference of the 'scientific mind' for its own products, in obedience to which Nature has to be reduced to zero-expressions.

It would be out of place to attempt to argue what is in effect a fundamental proposition in cosmic theory. But it should be pointed out that as a positive dogma it is quite out of place in textbooks intended for the student : out of place, that is, as a detached proposition apparently of the order of significance of a question of constitution or isomerism.

To consider for a moment the most prominent external characteristic of living matter, that is, essential and infinite variation and differentiation of form, this material property is correlative with adaptation, and in the higher types of life is measured by intelligence. The intelligence of the animal, a visible aggregate of compounds more or less exactly definable by the chemist, is thus presented to the ordinary student as the organic result of a property of ultimate matter, of the same order as that which

determines crystallisation. The issue of materialistic as against spiritualistic philosophy which is really involved in such apparently neutral assertions is of enormously wider dimensions than that of a side issue of chemical philosophy, and irrespective of the merits of the question so raised, it is not reasonable to innoculate the student mind with a forced perspective of fundamental relations.

The zero-expression, which is a postulate of the materialist, appears to be the equivalent of the fact that there is no numerical expression for form or structure in the sense of this discussion : it eludes our measurements and terminology. Having no definition as matter and no measure in terms of energy it is of zero significance. To concede this procedure is to suppress the Biologist as such, or at most to allow him a limited grazing ground, tethered by the chain of materialism to the centre defined by chemical philosophy.

But it narrows the objective of chemical investigation. If we revert to the textbooks as representing the general perspective of the science, the student would form from them his conclusions, in the terms of this brief exposé, that the fundamental chemistry of starch and cellulose is the chemistry of dextrose : the colloidal forms of these compounds are the expression of the mass aggregations of large and complex molecular units : the synthesis of dextrose from its elements having been effected, this logically involves in process of time the synthesis of the complex polyanhydrides : the morphological characteristics of these bodies are negligible, since they involve no changes of the matter constants, and have ascertainably no thermal or enefgy value.

On the contrary side the position may be thus stated. Notwithstanding the synthesis of dextrose, we have but little knowledge of dextrose matter, that is, of dextrose as it exists. We know little even of the mechanism of its resolution into alcohol and carbonic anhydride by ferments, though an approxi-

mately quantitative effect, and probably under more frequent observation and control by exact methods than any other phenomenon or reaction.

We know less of the bioses and the typical cane sugar.

Starch, though exhaustively studied in relation to its most characteristic break down to dextrine, maltose, and dextrose, is still less known. It is a typical colloid, and its actual constitution is involved in the general theory of the colloidal state, to the elucidation of which a fuller investigation of starch and starch products directed to this particular end must contribute.

. The same may be said of cellulose *a fortiori*. Lastly, there . are the special features of . form and structure superimposed upon the amorphous colloid. In systematic investigations these factors cannot be kept out of consideration.

It is probable, therefore, that progress from this basis of incomplete knowledge means a potentially large development of our current science. It is a matter to approach from the purely objective standpoint, and not to prejudge, either as a whole or in sections, from our present level of clear vision.

In our previous work we attempted to diverge from fixed ideas, applied to cellulose, by a definite suggestion that cellulose is not an aggregate of molecules with the dextrose constitution or configuration : that the colloidal state expresses a fundamental variation or differentiation of ultimate matter, that is, involves the ' molecule ' or reacting unit. Although carefully following the literature of the rapidly specialising subject of colloids, we were not able to draw upon it for any very substantial support of our hypotheses in relation to cellulose.

We are now in possession of the monograph of Wo. Ostwald, 'Grundriss der Kolloid Chemie' (see Bibliography), an important and opportune publication, not merely for the intrinsic interest of its matter, but as a comprehensive guide-book to the new borderland territory. This book has the merit of integrating contributions of matter of a diversified range, and

indicating the lines of convergence to a general theory of the colloidal state. But it has defects which we may be allowed to point out without detracting from its merits. It is an exhaustive bibliography, but the author has allowed himself no free play as a critic; the result is, to employ a topical description, somewhat colloidal.

In the next place, it is difficult to imagine a systematic study of colloids with starch and cellulose excluded. Ostwald barely mentions these bodies, notwithstanding that they are the very prototypes of the 'natural' colloids; moreover, they present a graduated series of structurally organised types, and not only are predominant in the 'natural' world, but in arts, manu-. factures, and generally the world of human existence.

This is to produce the play of 'Hamlet' with the part of the Prince left out. But the omission is not a matter of mere bulk or massive importance; starch and cellulose, by which we may comprehend the entire range of carbohydrates, are peculiarly marked out by their special chemistry as the basis of a deductive investigation of the colloidal state.

This view, suggested in our previous work, appears, moreover, particularly obvious, so that a reiteration of the grounds from which the conclusions proceeded may be dispensed with. It is, we may remark, emphasised by Otswald's treatise quite as much by the omissions as by its positive conclusions as to the colloidal state of matter. If we say 'positive' it is not intended in the sense of emphatic or definite.

Ostwald does in effect conclude that no physical measurements afford any valid evidence as to molecular dimensions or weight in the case of colloids; but he only vaguely suggests the general underlying cause of colloidal properties and effects, that is, the exaggerated development of 'specific surface' or the distribution of matter in two dimensions at the expense of the third.

This comprehensive inference to become a positive, definite,

working hypothesis in a deductive investigation requires application in a region where the subject-matter can be varied and at the same time controlled. This is particularly the case with the reaction changes of starch and cellulose, many of which are quantitative, and more especially is this true of synthetical reactions which take place conformably with general stoichio-metrical ratios, and therefore provide a series of definitely variable points of observation of very wide range.

On the general inference that the colloidal state is directly conditioned by a particular relation of surface to mass, it is left open as to whether this cause is operative in the molecular or polymolecular region. The more generally current view is that the colloidal state is a condition of matter in which large molecules of complex constitution are aggregated to ' physical ' units of variable dimensions ; it is left as an entirely open question whether the polymolecule is to be taken in any sense as the reacting unit, and on the special point under consideration, whether the surface-mass ratio affects the reacting unit in the chemical sense or the ' physical ' polymolecule.

It is evident that to avoid metaphysics and mere speculation we require a basis of exact investigation directed to fundamental points. Much of the investigation faithfully recorded by Ostwald (loc. cit.) is in the region of proximate qualities and effects, phenomena of so-called ' adsorption ' compounds, coagulation of colloidal solutions, etc.

On the other hand, fundamental properties and effects must be involved in problems of density and solution density : of thermal relations in (a) changes of volume and dimensions, (b) specific heat, (c) heat of reaction, and generally in the relations of cellulose, starch, and derivatives to the forms of energy, heat, electricity, and light.

Ground has been broken in these directions of research, and interesting relations have been disclosed by investigations which, however, are only superficial.

Systematic investigations will require an extraordinary perfection of experimental method, the colloidal state introducing unusual complications.

Lastly, we have to notice the relations of cellulose, in the broad and inclusive sense of the term, to biological science. We have few special contributions of research from this province. We have searched a recently published, general and exhaustive treatise, 'Biochemie der Pflanzen' (Czapek) (see p. 97), for evidence of progress in solving fundamental questions, as for instance, the problem of assimilation. For the original photosynthesis of organic matter, and primarily of the carbohydrates, science appears to have adopted formaldehyde as its non-nitrogenous 'protoplasm'.

But the potentialities of formaldehyde assumed as the first product of reduction of carbonic anhydride have not taken us very far in formulating a self-consistent scheme or mechanism of carbohydrate production in the plant. There is an obvious alternative in the monocarbon group, of synthesis from formic acid. The acid may be presumed as the first product of deoxidation of carbonic anhydride, but there does not appear to have been any serious suggestion of a direct function of the acid, and none of a possible mechanism. This introduces the general relation of the carboxylic acids to plant life and problems which have been investigated from time to time.

This imposing work, which is manifestly a faithful exposé of the state of development of the science of plant physiology, produces on the critical reader the general impression, that while the science has progressively formulated certain main principles of the constructive life of the plant cell, and of the conditions of its equilibrium with the destructive agencies with or against which it has to struggle, it has attained no grasp of the actual mechanism of any one of the processes the results of which are evident on a massive and colossal scale.

To select the most prominent of the problems—the synthesis

of sugars and starch and the entire range of carbohydrates, together with the elaboration and differentiation of cell and fibre tissue substances ; the formation of oils in seeds and fruits, and their general relation to assimilation ; chlorophyll and its functions ; the aliphatic carboxylic acids and their relation to assimilation ; the mineral constituents of the plant cell, and secretions and their relation to organic function,—these are all the subject-matter of elaborate and long-continued researches, and the phenomena are very fully characterised but on a basis largely of statistical observation.

Of exact knowledge we have only the beginnings, and the following extracts from Czapek's work may be reproduced in illustration :—

(p. 583) **Formation of cell membrane.**—Although the problem of the origin of cell membranes has been exhaustively studied by histologists, of whom we may mention Mohl, and later Pringsheim, and although in recent times the subject has been enriched by interesting experimental and theoretical studies, we are bound to say that we are very far removed from the position of successfully applying chemical methods to this eminently chemical problem.

(p. 134) **Oil and fat formation in ripening seeds and fruits.**—Of the processes concerned in fat formation in the ripening of oily seeds, including also the same phenomena in the flesh of the olive (fruit), our knowledge is extremely imperfect. That the unripe oily seed contains starch in abundance was known to older investigators, Meyen ('N. System Pflanzen Physiologie,' vol. 22, 1838, p. 293), Mulder (' Physiologische Chemie,' 1844, p. 269).

At this date we know little more. All fatty seeds in unripe stages contain various carbohydrates and sugar but no oil, and with ripening there is an increasing storage of oil *pari passu* with reduction of carbohydrates and starch.

Even on purely histological points much remains to be cleared up with regard to the phenomena of oil formation.

(vol. ii., p. 446) **Biochemical relation of the vegetable acids.**—Liebig's view that the organic acids are intermediate stages in the photosynthetic production of sugar from carbonic anhydride has proved with time less and less tenable. There have been very few investigators in later days who have favoured the Liebig theory, but we mention the researches of Brunner and Chuard ('Berl. Ber.' 1889, 19, p. 595).

(vol. i., p. 294) **Carbon assimilation and sugar formation in fungi and bacteria.**—In presence of the problem of carbon assimilation by the lower organisms in the absence of sugar, we are in a territory of inexhaustible experiment which up to the present has only provided first suggestions towards the attainment of generally valid conclusions.

(p. 507) **The cell membrane of bacteria.**—As a fact the latest researches show that all statements concerning the accounts of 'cellulose' in the cell membrane of bacteria are questionable and require revision.

(vol. i., p. 572) **Cutinised membrane.**—We may state that our knowledge of the phenomena of cork formation is so fragmentary that, e.g., it is still doubtful what carbohydrates, if indeed any, are present in cork.

A full bibliography of this subject is to be found in Czapek's work, together with a judicial exposé of the collateral questions which group round the main problem, Are the naturally occurring carboxylic acids upgrade or downgrade products? It is evidently possible to derive them from progressive deoxidations of $n \cdot CO_2 + m \cdot H_2O$ with synthetic union of residues, and the series of 'vegetable' acids have been thus accounted for as products of direct synthesis.

On the other hand, they may be regarded as products of respiratory combustion of carbohydrates, and downgrade products of variable occurrence with no fundamental relationship to assimilation.

In view of these generally *indecisive* results of physiological investigation on the one hand, which well express the elusiveness of the processes of cell life, and on the other, the vague generalities of chemists who would reduce ' organic ' chemistry to its simplest terms, carbonic acid, water, ammonia, it is necessary to construct a more positive intellectual position, and as a preliminary to form some conclusion as to whether laboratory views of synthesis, based upon fixed mental pictures of molecules, configuration diagrams, are not rather an impediment to progress in plant physiology unless complemented by views giving expression to a different order of mobility, lability, or plasticity ·of matter such as must obtain in the plant cell.

Since, moreover, it is evident that the arena of vital processes is colloidal matter, there is a suggestion that it is a preliminary necessity to inquire into the probable relations of the molecular to the colloidal conditions of matter. This certainly has not been attempted by the chemists in investigating plant products, since they not only apply molecular methods to colloids, but attach no positive meaning to their obvious failure. They appear to treat them as anomalies of passing significance, ultimately to be resolved in terms of 'molecular' science, i.e. the molecules which are the foundation units of ' organic chemistry '.

This prejudice, we think, obtains more widely than might be inferred from the general recognition of the infinitely constructive capability of the plant cell, with the collateral recognition that this capacity represents a chemistry *sui generis*.

Conversely, biologists are somewhat neglectful of progress of chemical investigation of plant products, and in no direction is this more clearly shown than in the treatment of the celluloses and ligno-celluloses. Thus in his ' Biochemie,' Czapek reproduces in full his own investigations of the constitution of the ligno-celluloses, or wood substance, but appears to be unaware of what has been established by thirty years' researches

on this subject, or of any failure to premise, from the results obtained by previous investigators, a critically defined basis of investigation.

To a student of the subject, aware of its present stage of development, any experimental contribution to this constitutional problem to have critical value must be founded on methods involving reactions which are simple or at least quantitatively defined, and, more especially, the relations of products of resolution to mother substances require to be simple.

Czapek attacks the highly complex, colloidal ligno-cellulose under conditions of an obviously complex reaction, and obtains a fractional proportion of a product which he regards as a · chemical individual, closely related to the parent substance. This product, ill defined and of doubtful relationship, is theoretically and speculatively treated as characterising the lignone groups of the ligno-celluloses. and under the term 'Hadromal' is going the round of technical literature.

A very slight critical inquest of the product in the laboratory would suffice to show that it has no simple relationships to the structural colloids of the parent substance, and is only one of scores of potential products of their resolution. We deal with this matter subsequently (p. 107).

But while giving prominence to a reaction, and conclusions which will be found on examination to be out of all proportion, there is no adequate treatment of two quantitative reactions of resolution of fundamental import, viz. the chlorination of the ligno-celluloses and their interaction with bisulphites. As we shall also have occasion to deal with these reactions in a subsequent particular discussion, we merely mention the omission as complementing the suggestion that biologists for really progressive investigation require to strengthen their critical grasp of chemical science, especially in these sections which deal with proximate material constituents of plant life.

On this very general theme it may not be out of place to

point out *en résumé* that our subject-matter, according to those perspectives, viz. of (*a*) the natural order, (*b*) the world of human life, (*c*) the system of natural sciences, takes a very different relative position.

Bulking largely in (*a*), having perhaps a more predominant importance in (*b*), in (*c*) it is regarded as a mere side issue of a sectional subject.

If, on the other hand, the colloids as such are to yield to systematic investigations, and to give us in turn a fully developed exact science, or chapters of exact science, which is certainly probable, it is also probable that the celluloses will contribute more than any other section to such development, and reciprocally, its position in the scientific order may in the near future be very different, even of analogous importance to that under (*a*) and (*b*).

CHAPTER II

The characteristics and definition of a normal cellulose are discussed in relation to certain special applications of cellulose, and also in relation to 'normal' processes of isolation from fibrous raw materials. The recent investigations of M. Renker (Berlin, 'Dissertation.' 1909) are fully noticed.

The exhaustive or ultimate hydrolysis of the normal cellulose (to hexoses) has been further studied by Ost and Wilkening, who consider that their results finally establish its quantitative resolution to dextrose.

Acetolysis is the term applied to resolution of complex carbohydrates by acids in presence of acetylating reagents, which simultaneously esterify the OH groups. A biose, cellobiose, is obtained from cellulose as an ultimate product, and establishes a further point of constitutional analogy with starch. Specific volumes and solution volumes of starch and cellulose are the subject of preliminary investigations by the authors (with J. F. Briggs), and certain anomalies are disclosed which would find an explanation in the assumption of a cyclic configuration of the component groups.

NORMAL CELLULOSE.

THE term 'normal cellulose' is one which we and others have used as self-explanatory. It may, however, be opportune to consider an exact definition, as the matter in the form of the question, What is the normal cellulose? has recently come into prominence. The well-known heat test for high explosives (nitro-cellulose, nitro-glycerin) involves the reaction of nitric oxide with potassium iodide, for which the convenient carrier is a bibulous paper. The paper usually adopted is a 'pure'

chemical filter paper. But in revising the conditions for an ' official test ' the expert authorities have found it necessary to go behind the superficial claims of cellulose papers to be regarded as 'pure'. Such papers, highly purified from the one point of view, have been found to vary considerably in regard to the condition of ' purity ' of the cellulose.

It is clear that an insoluble colloidal organised substance can only be purified by the action of solvents on its impurities ; these may be solvent liquids, or reagents which attack the impurities and convert them into soluble forms. The cellulose is thus a residue from such treatments, and from what we know of cellulose it does not remain inert under treatment ; the residue therefore is the original cellulose free from special impurities but changed more or less in constitution.

The original cellulose, which we will presume to be cotton, is without doubt not a simple or homogeneous substance. As elaborated and matured in the plant, we must assume the influence of time, that is, a time factor of cellulose constitution, and if we form some mental picture of the cotton substance, it must be that of an essentially variable aggregate whose composition is influenced, not only by time, but by all the conditions of growth. Still in the region of inference, for which no verification is yet possible, we may affirm that the ultimate constitution of cellulose is remote from these influences, and that they determine variations only in the proximate configuration of the aggregate.

The order of such variations may be compared with that of a dilute solution of an electrolyte, in which proximate configuration of the solute must vary with every change of conditions. The consideration of such variations enters but little into our ordinary systematic chemistry, but they are of obvious moment in the practical investigation and treatment of colloids in which we cannot ignore the aggregate.

The chemical process of the treatment of raw cotton for

2 *

the isolation of a pure cellulose may very well be calculated to lessen rather than exaggerate the variations of the parent substance.   A 'normal bleached' cotton may represent a nearer approach to a homogeneous substance.

In applying the term 'normal' to the bleaching process we have in view the ascertained limits of resistance of cellulose to chemical treatment, chiefly alkaline hydrolysis and oxidation ; resistance in this sense must be measured by conservation of substance (weight) and chemical inertness or non-reactivity of product.

From this comprehensive point of view, considering, that is, raw material and its proximate composition, the process, *and* product, we have always taken the calico printers most highly purified cotton cellulose as the nearest approach to the 'normal cellulose'.

On the other hand it is very often assumed that other forms of 'highly purified' celluloses have equal claims to the description as normal, notably the chemical filter papers of Swedish or German manufacture, or 'surgical cotton' wool (Verbandwatte), which very frequently figures as the basis of scientific investigations of cellulose and derivatives.

Reverting to the investigations of the explosives experts, they have found that some of the variations of the heat test *results* may be referred to a contribution of effect from the test papers themselves, which have been made by treating 'chemical' filter paper with a solution of iodide of potassium and 'pure' starch, drying and storing in stoppered bottles.   It has also been ascertained that these chemical filter papers do not represent a cellulose of the chemical inertness of the normal cellulose :   they contain easily oxidisable matter, celluloses chemically degraded by oxidation or hydrolysis, and consequently an undue proportion of alkali soluble components.

As a result of these investigations, and taking into account also the facts previously established as defining purity and

degree of purity of celluloses for conversion into nitrocelluloses, the following points have been formulated as a specification of essential chemical requirements.

These are tentative proposals and subject, of course, to modification. They are, however, eminently instructive as a technological document and are reproduced as such :—

FILTER PAPER.

SPECIFICATION No. 54 A.

The paper for filtering nitroglycerine and for making heat test paper is to consist entirely of pure normal cotton cellulose of strongly resistant quality and free from any loading or sizing.

During manufacture the paper is not to be submitted to artificial heat of any kind.

The paper is to have a smooth white surface, and both sides are to be as nearly alike as possible.

The average length of the fibres is to be 2 ± 0.5 mm.

Ten sheets when measured with a Ciceri Smith's patent fixed pressure micrometer are to have a thickness of 1.80 ± 0.2 mm.

The weight of the paper per cubic centimetre is to be 0.45 ± 0.05 gram.

The last treatment in its preparation is to be a thorough washing with pure distilled water and subsequent air-drying in a pure atmosphere.

The paper is to be perfectly free from alkalies and alkaline earths and also from all traces of chemical or other impurity, particularly acids, chlorine, and peroxides.

The ash in the paper is not to exceed 0.10 p.ct.

On boiling with 3 p.ct. caustic soda solution for sixty minutes, the paper is not to lose more than 7.5 p.ct. of its weight.

When heated for fifteen minutes at $100°$C. with Fehling's solution, diluted with twice its volume of boiling water, it is not to produce more than 1.25 p.ct. of its weight of cuprous oxide (Cu_2O).

It is to be supplied in sheets 50 cm. long by 15 cm. wide, and each 100 sheets packed separately in a hermetically sealed tin case closed by a tear-off strip.

Date: 27 March, 1911.

Co-operating with the specialists it was of interest to see how far the calico printers' types of specially bleached cotton would conform to this specification, which is obviously intended as a definition of a normal cellulose.

We obtained from the Calico Printers' Association, through Mr. W. Kay, the chief chemist, selected specimens typical of specially varied standard chemical treatments.

The description of the specimens, together with the results of the tests applied to test their degree of conformity as celluloses with the above specification, are recorded in the subjoined table :—

No. 1. Standard ' Madder ' bleached calico.

  ,, 2. ' Madder ' bleached, afterwards malted.

  ,, 3. Madder bleached, afterwards re-boiled in alkali.

  ., 4. ' Satteen ' (Egyptian cotton), mercerised in ' grey,' afterwards bleached without lime boil.

  ,, 5. As No. 4, but afterwards malted.

Results of tests of above five specimens :—

Solubility in boiling 3 p ct. NaOH	Copper deduction (Febling's solution	Ash	Dyeing test (basic dyes)
3·41	0·45	0·096	Light, medium
3·14	0·43	0·038	Light
1·66	0·39	0·150	Light, medium
4·23	0·54	0·110	Light, medium, uneven
2·39	0·35	0·090	Light, medium

No ' active ' oxygen or chlorine present in any specimen : a l contained traces of saline chlorine.

We ourselves examined the specimens by a laboratory method which has been more particularly devised in the testing of cellulose as raw materials for the viscose processes, but which we are about to discuss briefly in reference to the methodical diagnosis of a normal cellulose   It is based primarily on

resistance to the action of caustic soda solution at mercerising strength. A normal cotton cellulose loses no weight under mercerisation (17·5 p.ct. NaOH). In the case of celluloses which contain alkali soluble derivatives, the alkaline extract is treated with acid (acetic), and reprecipitated products collected and estimated (β cellulose) The cellulose is fractionated by this treatment into :—

α Cellulose : insoluble in NaOHAq (17 p ct. NaOH).

β   ,,   soluble and reprecipitated by acids.

γ   ,,   not reprecipitated : permanently soluble.

The following are the results of treatment of the specimen celluloses one and three according to this method :—

	α Cellulose	β Cellulose	γ Cellulose
No. 1	99·5	0·4	0·1
,, 3	100·0	0·0	0·0

These results are referred to original dry ash-free cellulose.

Tested in terms of either method, therefore, these forms of cotton cellulose are a satisfactory approximation to the chemical ' normal '. Being industrial products they are readily obtainable, and in cases where cloth or yarn is the form of cellulose required, and in cases where the spinner's twist of the yarn is of no moment, they can be recommended in preference to any other form.

But a cloth or yarn fabric is unsuitable as a form of cellulose carrier of the iodide starch reagent.

The paper texture and surface are required, and in the unsized condition of a bibulous paper. It will have been noted that the specification of the special *paper* carries certain added conditions applicable to this structural form.

The chemist may not at once recognise the complications introduced by this change of form, having regard to the identity of the material basis of fibrous cellulose. They are complications of limitations.

In the first place, a paper of any form cannot be mechani-

cally handled as can a cloth or yarn. The 'wet strength' of a blotting or bibulous paper is a fraction only of its dry strength, which from its special texture is the lowest in the range of papers.

To the sheet of paper, therefore, we cannot apply chemical processes of purification ; the conversion of raw material into 'normal' cellulose would therefore precede the mechanical processes of the papermaker.

In the second place papermaking has its industrial basis of costs ; the paper industry, so far as it uses cellulose of the 'A' or long fibre class, can only obtain these economically in the form of 'waste' material, either wastes of the textile industries, or general wastes such as rags and old papers. For the highest class and highest priced papers, selected 'clean' wastes are available, but even these require processes of chemical purification, as for instance from sizing, and dressing materials incidental to spinning, weaving, and finishing.

Hence, from our present point of view, papers of reputed 'purity' will be found to represent, *qua* cellulose, more or less divergence from the normal.

Outside economical considerations, ordinary raw, i.e. unmanufactured cotton, treated on the lines of the calico printers' special bleaching process, would furnish an approximately normal cellulose paper, therefore a solution of the problem under discussion.

But we may here mention that the economic limitation of the use of unmanufactured cotton is in process of being removed by rendering available the hitherto waste fibre of the original cotton seed. In removing the long staple cotton from the seed by the mechanical process of 'ginning,' there is a residue of short fibre remaining attached to the seed envelopes. As the raw material for cotton seed oil and cake industries the residue of 'hulls' retains a superficial 'down' of short cotton fibre amounting to from 15 to 22 p.ct. by weight, and there

have been numerous attempts to separate and concentrate this fibre by mechanical processes. Seeing that there is a potential source of supply of the short fibre of 200,000 to 300,000 tons from American seed alone, the technical problem is important. Recently invented machines have in effect produced a separation of fibre from shell, or residues of cellular seed tissues, so complete that the product contains over 90 p.ct. of fibre and yields 82 p.ct. of 'pure' cellulose on treatment by 'normal' laboratory methods.

This may seem irrelevant to the present discussion, but the relevancy is nevertheless direct.

Taking the extreme cases of this raw material, the original with 20 p.ct. of potential fibrous cellulose, the new concentrated product with 90 p.ct. and considering them in relation to the technical problem of cellulose isolation, and without regard to costs ; in the one case we have to attack and remove the 'shell' residues or seed tissues, in the proportion of 400 p.ct. of the cellulose to be isolated, in the other 10-11 p.ct. The seed tissues are a ligno-cellulose complex and require severe alkaline treatment for conversion into soluble products.

The difference of the intensity of the chemical treatments in the two cases is evident, and the difference of concurrent attack of the cellulose is also evident. Thus the concentration of cellulose by purely mechanical means affects not only the chemical economy of the process of treatment, but also the character of the product and of course the costs of production.

The growing supply of cotton hull fibre appears therefore destined to solve a special problem in cellulose industry of mainly scientific import, at the same time that it contributes a new supply of economic raw material for the paper trade generally. We return to this question in a subsequent chapter.

In regard, therefore, to the problem of a normal 'pure' or purified cellulose :—

As it is necessarily a residue from chemical treatments to

which it is only relatively inert, these treatments must conform to a normal standard. These standards have been fixed in the process of evolution of industrial processes, but require some revision in relation to our more exact knowledge of ' normal ' quality : defined, that is, by quantitative measures rather than the qualitative observations of the calico printer.

We therefore have to consider finally which of the proposed qualitative tests should be adopted as defining the normal cellulose or approximating thereto. It is evident that the specification of celluloses for ' nitration ' for explosives is well designed, but it will be admitted that the numbers fixed as a reciprocal measure of resistance to alkaline hydrolysis and oxidation are arbitrary, as are the conditions of intensity and duration of the processes selected.

The arbitrary features of the scheme would disappear by studying the processes exactly varied as to intensity or duration. If such results were plotted in diagram form it would no doubt be easy to see, in a given cellulose, where the relative non-reactivity of the normal cellulose asserted itself, and a line would be drawn separating the contribution of effects of the lower or modified celluloses.

It is possible that in already published researches the material already exists for such a revision, both in the case of the processes of alkaline hydrolysis and alkaline oxidations $Ca(OCl)_2$.

To make the scheme complete, a complementary study of acid hydrolysis and oxidation under acid conditions would be required.

The elaboration of such a scheme may well be commended to the technical schools showing an active interest in cellulose investigations.

While, however, the matter remains on an empirical and somewhat arbitrary basis, we suggest that the mercerisation reaction affords a comprehensive measure of the normal.

It is established that cotton cellulose, approximating to the normal on the calico printers' tests, suffers no sensible weight changes under this severe treatment, which in the case of other celluloses collectively attacks and dissolves the modified or lower-grade celluloses, whether of natural origin in the plant, or resulting from processes of hydrolysis and oxidation by artificial treatment.

Incidentally, we may remark that the mercerisation followed by reaction with carbon disulphide, generally the viscose cycle of solution and reversion to insoluble cellulose, is also a quantitative phenomenon, and in experienced hands affords valuable complementary indications of associated colloidal characteristics. This would be included in special investigations.

To sum up the discussion :—

The normal cotton cellulose may be defined in terms of resistance to hydrolytic and oxidation changes, which may be tested under conditions more or less arbitrarily selected as regards intensity and duration of action, but must be fixed as constants.

It may also be defined in terms of the mercerisation reaction, in which it maintains approximately constant weight. This latter method is the more simple and convenient.

Incidentally, the cellulose should be examined for 'purity' for which a comprehensive test is exposure to chlorine gas; ligno-cellulose residues combine, and the products give coloured derivatives with sodium sulphite; proteid residues give chloramines (Cross, Bevan, and Briggs, 'J.S.C.I.,' 1908, 27 ; Cross, Bevan, and Bacon, 'C.S.J.,' 1910, 97, 2404) in which the combined chlorine remains 'active'; generally oxidisable matter gives rise to the production of HCl which may be estimated.

NORMAL METHODS OF ISOLATING AND PURIFYING CELLULOSE.

In the previous section we have discussed the term normal cellulose, chiefly in relation to cotton cellulose and the forms in which it is generally available.

We have indicated that attention should be paid to the conditions of the processes of isolation of the ' pure cellulose ' from the raw cotton (or fabric).

It is not established by the discussion that the special processes of the calico printer (madder bleach) conform with what we might define as normal conditions of treatment, notwithstanding that it yields an approximately normal cellulose. It is clear that a normal process would be based on specific reactions and conversions of the impurities to be eliminated into soluble derivatives with ascertained minimum action on the cellulose.

The impurities of the cotton fibre in the raw state are the proteid matters, a complex of fat and wax constituents, carbo-hydrates of the pectic groups, and ligno-celluloses in minute proportion.

The alkaline treatments of the calico printer have obviously complex relations to these diversified constitutional types : involving resolution or break down, by processes of hydrolysis and saponification, together with effects of solution peculiarly characteristic of colloids.

The process is therefore one of general and diversified attack, it is not direct in the sense of a specific action capable of quantitative definition. In the positive sense, therefore, not normal ; it is only in the negative sense of minimum action on the cellulose that it may conform with the definition. We are not aware that this point has ever been specifically investigated, other than as a practical, technical problem.

There is scope for research work in this direction which would require to follow up the more comprehensive characterisation of the normal cellulose in the schemes on pp. 30-32. This again may be commended to the technical schools as affording, moreover, a staple routine subject for the systematic training of students.

The accumulation of quantitative results under such a scheme would be a valuable contribution to the subject.

But at the same time it is obvious that the laboratory cannot take its lead from the works, and the alkaline process of 'saponification,' to use the general term, should be varied on the basis of general principle, and without regard to any immediate 'practical' considerations.

Thus the substitution of alcohol for water as the solvent and reaction medium is an obviously necessary variation, affecting the intensity and direction of action of the alkali, on the impurities, and possibly limiting the action on the cellulose.

This variation of the chemist, which is open to an evident criticism of the 'practical man' in terms of the usual formula 'what is the good of it?' is a necessary factor of the full investigation of a normal cellulose, and a further evidence, we think, of the importance of this discussion in showing that we are still content with empirical and conventional foundations for our technology of cellulose.

But this discussion leads us into a subject of complementary bearings upon the general question, viz. that of the various processes of estimating cellulose in the laboratory. The diversity of process and result reveals the fact that chemists have not based their work in this direction on a preliminary critical discussion of the question in its two complementary sections: What is a normal cellulose? and what is a normal process of isolating cellulose from a given vegetable substance?

We have dealt with these questions in our investigations and in our previous publications, and we are relieved from the necessity of reiteration by the appearance of a very important contribution, a general critical study of quantitative methods which we proceed to notice :—

UEBER DIE BESTIMMUNGSMETHODEN DER CELLULOSE.

By M. RENKER ('Inaug. Diss.,' Berlin, 1909).

It is a comparative and exhaustive study of the various methods which have been proposed for the isolation and quantitative estimation of 'cellulose'.   The results of this investigation we shall reproduce in full abstract in elucidation of the questions before us, which although present to the mind of the author, and directing his investigations and criticisms, are not formulated in specific terms.

In setting out the requirements to be fulfilled by a process of cellulose estimation the author postulates :—

1. It must yield a cellulose of maximum purity, free from lignone (residue) and all coloured compounds.

Mineral constituents are negligible in the sense of affecting the cellulose problem, they can either be estimated or accounted for and removed by solvents.

Cellulose purity must, however, include freedom from products of decomposition (though colourless), e.g. hydro-cellulose, oxy-cellulose.

2. That process must be critically judged to be the best which gives the highest yield of such pure cellulose, with ascertained minimum of change in the cellulose attending the process of isolation.   A direct measure of such change is loss of weight of the pure cellulose product when again subjected to the series of treatments.   This should be a minimum.

3. Incidentally, in reference rather to technical exigencies the process should be rapid and simple.

On this basis the author has critically examined some twenty of the methods which have been specially devised and more or less widely adopted, and in relation to four raw fibrous materials representing types of technical and scientific importance, viz. pine wood (shavings), jute (papermaker's half stuff), 'sulphite'

wood pulp, and raw cotton, but mechanically highly purified and free from non-fibrous admixtures.

In following sections the author deals with points of importance in the second degree, viz. (1) the drying of raw materials and products. The investigation of the various conditions of drying at limits of temperature 40-98°, 98-115°, 115-150°, compared with the vacuum exsiccator, and with the effects of a stream of warm desiccated air, led to some observations of importance in the sensitiveness of the isolated cellulose to temperatures of 115°.

2. The various tests to be applied to the isolated celluloses to determine degree of purification, and ultimately of conformity with the definition of a ' pure ' cellulose.

After this clear exposition of preliminaries follow the records of the investigations of the methods under the following scheme of classification :—

A. Methods of isolation by processes of hydrolysis.

B. By oxidants, including the halogens.

C. By special methods, as e.g. by the action of phenols, (Buhler, 'Chem. Industrie,' 1903, 138 ; R.P., 94, 467) and by various methods of applying the cuprammonium reagent (Muntz, Hoffmeister, König).

The author's conclusions are contained in a short summary with a table of results which are experimental mean numbers for the maximum yield of cellulose, the final criterion adopted. In view of its importance, and to preserve its independence, we give a literal translation.

' These investigations show that an absolutely accurate method of cellulose investigation has not yet been devised.

' Of all the methods and reagents proposed for the purpose it may be said, either that they attack the cellulose, or that they fail to give a pure lignin-free product from the more highly lignified fibrous materials. A comparison of the various

methods is given in the following tabular summary of quantitative results, i.e. of cellulose yields :—

Method	Yield of Cellulose from typical Raw Materials as below :			
	Sulphite pulp	Jute	Wood	Cotton
Glycerin sulphuric acid (König) . .	74·15	—	—	—
Chlorination—Cl. gas (Cross and Bevan)	97·9	84·5	60·55	97·85
„ Cl. Aq. concentrated .	97·65	83·4	57·1	94·7
„ Cl. Aq. diluted . .	98·0	81·1	—	96·8
Bromination, Br. Aq. (H. Muller) .	98·1	83·3	57·95	97·1
„ „ (Klason) . .	96·6	80·8	51·85	95·45
HNO_3 Aq. + $KClO_3$ (Schutze) . .	98·05	79·2	58·1	96·95
HCl. Aq. + $KClO_3$ (Hoffmeister) . .	98·25	82·5	57·15	96·15
HNO_3 Aq. at 60°-80° (Cross and Bevan)	97·65	79·75	53·6	96·35
Nitrous acid and nitric oxide (D.R P. 204,460)	98·2	80·65	55·8	98·85
HNO_3 + H_2SO_4 (Lifschutz) . . .	—	—	43·35	—
HNO_3 Aq. + $KMnO_4$ (Zeisel and Stritar)	99·6	70·95	40·2[1]	93·25
$KMnO_4$ Aq. neutral	98·5[1]	87·4[1]	—	—
$KMnO_4$ Aq. and acetic acid . . .	98·25	83·6	—	97·6
$KMnO_4$ Aq. and hydrochloric acid .	97·9	82·9	43·0	96·65
Hydrogen peroxide	96·05	—	—	96·55
Sodium hypochlorite	97·4	83·4	50·5	96·8
Phenol (D.R.P., 94, 467) . . .	90·75	79·4	51·9	94·2

' The highest results of all the processes investigated is given by that of treatment with gaseous chlorine, according to the method of Cross and Bevan, but slightly modified in respect of the treatment of the chlorinated fibre (no NaOH added to sulphite solution).   This process has the additional advantage of the greatest rapidity and simplicity, except in the case of highly lignified substances as the woods.   But even here the manipulation, although tedious, is more expeditious than in other processes.

' It is an essential point to reduce the duration of exposure to chlorine to the minimum, necessary for full reaction ; beyond

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[1] Products imperfectly resolved : retain much lignone.   Method valueess as ' cellulose process '.

this point an attack on the cellulose itself is evident. The yield of cellulose is increased by cooling (with ice) and by treatment of the fibrous material after chlorination with aqueous sulphurous acid. Further, this process of Cross and Bevan has the advantage of a process accurately studied as a chemical process, and free from the complication of secondary reactions. The final product is free from oxy-celluloses, and of exceptional purity.

'In addition to this method there is also available for the estimation of cellulose in sulphite pulps, and the purer less lignified bast fibres, the process of oxidation (of non cellulose) by permanganate in acetic acid solution, which attacks the cellulose only slightly ; a portion, however, is certainly converted into oxy-cellulose. The process cannot be employed in the case of strongly lignified substances.

'Hugo Müller's method, in which also there is a very slight attack of the cellulose, and the product is of exceptional purity, involves too complex manipulation for consideration in connection with technical applications ; the same also holds for the processes of Schulze and Hoffmeister, which, moreover, give coloured oxidised cellulose products, and with inferior yields. These processes also present the great disadvantage that it is impossible to recognise any end point of the main reactions, and the contact of the substances with the oxidising reagent is prolonged beyond the time necessary for complete attack of the lignone, hence losses of cellulose which easily result.

'The nitric acid process of Cross and Bevan, although most simple and convenient, is not applicable for exact determinations, owing to strong action on the cellulose.

'The other processes investigated are also for a similar reason to be ruled out.'

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Upon this brochure we offer the general criticism that the experimental work has every evidence of accuracy, and the

conclusions are consistent. We observe, moreover, that the work is being generally recognised in the technical scientific world as of standard critical importance.

We have briefly to point out its direct bearings on the question of 'normal cellulose'. Referring to the classification of the celluloses ('Cellulose,' 1895, p. 78) the term 'normal' in the full sense is limited to the chemical prototype which is cotton cellulose.

In our previous discussion we have been rather comparing one form of cotton cellulose with another with a view to fix a normal standard, first of the product, and in the next place of the process by which the product is obtained, that is, isolated.

In this narrower sense also each class of cellulose would have its normal standard, and Renker's conclusions were in effect so defined in relation to the cellulose of class B. They refer to the process measured (1) by a 'net' quantitative effect (yield of cellulose), and (2) by the exactly defined quantitative relations of the main reaction. To show that this implied distinction is not always recognised, and therefore requires restatement, we may point out that the process of cellulose estimation based on chlorination has been criticised for the fact that *the cellulose isolated from the ligno-cellulose is not simple but contains an admixture of 'β' cellulose, a cellulose of 'furfuroid' characteristics.*

This cellulose, moreover, with a fundamental differentiation of its ultimate groups, is much less resistant to hydrolysis; in other respects, and in all general and typical characteristics, it is a cellulose. Its conservation under the process is thus a further evidence of the sharply defined lines of this main reaction, and of the limitation of the incidental hydrolytic reactions.

In other methods of mixed oxidation and hydrolysis the 'β' celluloses are attacked and dissolved. Hence the process of chlorination is *normal* in the sense that the reactions are quantitative, and strictly limited; the product in the case of the ligno-celluloses is a normal cellulose of its class (B), representing the maximum of original compound groups of the ligno-celluloses, fulfilling the definition of a cellulose.

In connection with the definition of a normal cellulose we have to consider a minor issue which has been discussed by various investigators, and from various points of view, that is, When is cellulose to be considered as hydrated? What are the hydrates of cellulose?

In regard generally to the combining relationships of cellulose to water, there are no differences of opinion as to the main facts, which, moreover, are quantitatively measureable. ('Cellulose,' 1895 : 'Researches,' I and II).

The normal cotton cellulose has its 'humidity' constant of 6 to 7 p.ct. in equilibrium with ordinary air; under alkaline treatment, and particularly mercerisation, the constant is increased, that is, the products resulting from such treatments take up, and hold a higher complement of moisture ; conversely, with acid treatments yielding 'hydrocelluloses,' these derivatives are lower in 'moisture' ('Chem. Soc. J.' 85, 691).

These 'humidity' constants of the cellulose series are thus essentially variable, also in any given product they represent a variable equilibrium with atmospheric moisture.

They are, however, *constants* in the sense of expressing definitely limited variations and fundamental relationships, the well-marked phases of differentiation which they express are constitutional ; they are associated with differentiation of function, and therefore of position of the characteristic CO groups of the C_6 unit, and the changes in the aggregate of groups are marked by extremes of structural effects. It is generally evident from the reactions that they can only immediately involve H_2O groups, and it is of importance to determine whether there are changes of composition of the ultimate units, that is, changes of elementary composition, or changes of the cellulose complex of a more general order.

From the extensive records of investigation of this highly complex series of derivatives, comprising 'oxy-cellulose,' 'hydrocellulose,' 'hydra-celluloses,' and a large number of naturally occurring products, it appears that we have no evidence of hydrolysis comparable with that of starch (through the dextrines) to maltose. This point of considerable interest and importance

has been very fully investigated and discussed, and we may refer the reader to the textbooks.

We may perhaps draw the general conclusion that the aggregate of the typical characteristics of cellulose is essentially an anhydride complex, and hydrolysis of ultimate groups in the ratio, $2n . C_6H_{10}O_5 + nH_2O = n . C_{12}H_{22}O_{11}$, implies the loss of typical characteristics and severance from the colloidal aggregate. In a complex such as cellulose it is clear that degradation changes of this kind must be highly complex, and would only be very imperfectly expressed in terms of elementary composition of the changing aggregate. Our conclusion, therefore, is rather a general deduction from the equally complex literature of the subject.

But while there is a general agreement as to the factor of hydrolysis, there is an issue as to the value to be assigned to hydration. In a recent publication which we notice subsequently at length (p. 81), H. Ost, with F. Westhoff and L. Gessner, deals with the subject under the sectional heading 'Die sogenannte Hydrat-Cellulose' (the so-called cellulose hydrate).

Ost has made elementary analyses of the extreme products of the alkali cellulose (cotton) viscose series : the 'reverted' purified celluloses (hydrates ?) were 'dried' at $125°$C. before combustion, or weighed for combustion in the air dry state, and the combustion figures corrected for loss at $125°$ (water).

The figures are uniformly those for $C_6H_{10}O_5$.

The conclusion drawn in the author's words is that 'Die Name Hydratcellulose keine Berechtigung hat' and in dealing by way of illustration with the starch-dextrin series, which also show the tendency to maintain the anhydride composition, these compounds are spoken of as anhydrides, with strongly hygroscopic properties. These properties are not accidental, but are probably referable to purely physical causes.

We do not admit these conclusions for very definite reasons.

The relationships of cellulose to water are of fundamental importance, and are a function of constitution in the chemical sense. The constants of humidity with their definite variations

are precise quantitative characteristics. Drying at 125° or any temperatures is a decomposition or dissociation of a hydrate, and not a mere removal of hygroscopic 'moisture'.

As a detail of criticism, we consider that 125° is too close an approach to the point 160° at which cellulose shows itself liable to structural and therefore obvious constitutional change. Under ordinary conditions, in presence of atmospheric oxygen, constitutional changes are determined in cellulose and cellulose derivatives generally, and special attention has been given to this point by Renker in connection with his investigation of quantitative methods (loc. cit.).

Incidentally, moreover, Renker has observed that celluloses separated by the methods investigated, when washed with alcohol previously to drying, retain, persistently, notable proportions of alcohol, even at 100°.

This combination of the cellulose with the monohydric alcohol is analogous to that with water. Such combinations are more definitely indicated, if not measured, by determinations of volume. The apparent specific gravity of cellulose in water shows a relatively large volume change; but comparisons with other liquids, notably alcohol and hydrocarbons, has revealed specific effects.

Upon hydration effects of this order depend a larger number of industrial operations of the groups of spinning (fibres), finishing (textiles), dyeing and printing (textiles), and papermaking. But it is evidently in the plant world that the hydrates of cellulose are of primary significance and function, and in face of this enormous range of hydration phenomena it is difficult to account for the supposed significance of the temperature of 125° and the elementary composition of the complex after sufficient exposure to this temperature.

From the point of view of the present discussion a cellulose 'dried' at 125° is not a normal cellulose, nor can the process of 'drying' at 125° be accepted as fulfilling the definition of 'normal' unless proved by investigation to be without effect upon the associated physical and mechanical properties of the normal colloidal complex.

That this is not the case follows not only from the laboratory routine, and technical observation, but from patent specifications which claim constitutional modifications of cellulose by exposure to high temperatures in contact with inert gases (D.R.P., 64,301, 1891, Chardonnet, D.R.P., 199,885, 1907, Berl.).

As a general conclusion from this discussion we have defined the term 'normal' both in its limited and its more extended application to cellulose. Considered, however, as a laboratory product, it is a residue of processes, and it is therefore necessary to take into account the probable effects of these processes in modifying the cellulose from the true normal, which is the natural normal.

Ultimately it is probable that we shall be in possession of a basis of comparison, and be able to differentiate these various figures in exact terms. It is necessary at this stage of evolution to formulate the fact of such variations in general terms, thus :—

'Natural normal'.	The cellulose complex, as it exists in the plant or plant substance.
'Normal pure cellulose'.	Cellulose isolated by chemical treatment, by processes ascertained to fulfil normal conditions. This may be a cellulose of any one of the groups of the accepted classification.
Normal cellulose, Normal chemical type	is the cotton fibre substance considered either as a natural or a normal pure substance as above defined.

CELLULOSE AS A CHEMICAL INDIVIDUAL.
CONSTITUTION.

The 'organic' relationships of cellulose are of two orders :—

1. With the natural and living world, in which it presents the characteristics of specialised form or structure.

2. With the scheme of chemical science, in which it is an aggregate or complex of simple groups of (supposed) known con-

stitution and configuration.   In the latter it may be regarded as a structureless colloid, and the problems presented are those of the proximate constitution of the complex, together with that of the ultimate groups into which it might be resolved.   •

In the resolution of cellulose by solution in sulphuric acid (Flechsig, Béchamp, and others), diluting and boiling, it has been generally accepted that the yield of dextrose is quantitative (see Ost and Wilkening, *infra*).

In view of the fundamental importance of these constants the subject has been reinvestigated, and we give an account of the experimental facts recently determined.

DIE VERZUCKERUNG DES ZELLSTOTFS.

H. Ost and L. Wilkening ('Chem. Ztg.,' 1910).

THE CONVERSION OF CELLULOSE INTO SUGARS.

The authors first notice the investigations of Simonsen (Z. angew. Chem., 1898, 219), the purpose of which was the industrial production of fermentable sugars from cellulo-es and from woods.   The maximum yield of 40-48 p.ct. dextrose calculated to anhydrous cellulose was obtained with highly dilute acids (0·5 p.ct. H_2SO_4), and for short periods of digestion at high temperatures ($175°$-$183° = 8$-10 atm.).   (These investiga-tions have been noticed and discussed in 'Researches,' I, 1901, p. 146.)   Later studies by Kirner (Z. angew. Chem., 1908, 2353), in which it was attempted to extend the limits of hydrolysis by the addition of oxidants, have confirmed Simonsen's results for the action of the simple hydrolysis and without increase of yield due to the joint action of oxidants.

The limit of hydrolysis is not merely due to 'condensa-tions' within the cellulose residue, but to reversion changes of the dextrose produced.   This direction of change is less pro-nounced at $120°$-$145°$, but decompositions result with produc-tion of lævulic and formic acids.   The following observations on pure dextrose indicate the rate of decomposition.

Concentration of Dextrose	Solution. H_2SO_4	Heated in Hours	Autoclave Temp. °	Dextrose recovered	
				Reduction	Polarisation
5	2	3	120°	91·4	91·0
5	2	8	120°	70·3	71·0
5	2	1½	145°	67·5	67·5
5	2	5	145°	28·6	28·9
				35·1	35·0

An experiment on exhaustive hydrolysis of cellulose under similar conditions, viz. six successive treatments with 1 p.ct. H_2SO_4 at 150°, each of two hours, gave a total yield of 44·3 p.ct. dextrose, of which 40 p.ct. was obtained in the second series of three digestions.

The disintegrated residue weighed 46 p.ct. of the original; it was dissolved in $H_2SO_4 . H_2O$ and hydrolysed by boiling, yielding a further 42·7 of dextrose p.ct. of original cotton.

The authors then proceeded to re-examine the question of total hydrolysis of cellulose under the conditions of the long-standing investigations of Flechsig ('Ztschr. phys. Chem.,' 1882-83, 913), whose results have been much questioned, and recently by Schwalbe and Schulz ('Berl. Ber.,' 1910, 916).

Flechsig's results are, however, in the main confirmed.

The conditions of treatment for maximum conversion require careful control. $H_2SO_4 Aq.$, of 65-72 p.ct. H_2SO_4, solution of the cellulose at ordinary temperatures (15°-20°) in 7-10 times its weight of acid, allowed to stand until no precipitate forms on dilution, diluted to an acid concentration of 2-3 p.ct. (H_2SO_4) and heated two hours at 120°.

The yields of dextrose estimated in terms of cupric reduction approximated to the theoretical for total hydrolysis to dextrose, viz. 111·1 p.ct.; but the figures for polarisation are inferior to those for pure dextrose, and there is an invariable formation of acid bodies.

The quantitative results in the tables subjoined are of considerable importance. The organic acids are expressed in terms of percentage equivalent of H_2SO_4.

TABLE I.

SOLUTION OF COTTON CELLULOSE IN 72 P.CT. H_2SO_4 AT 15°-20°.

	Dissolved			Diluton to		Heated		Yields		
	Cellulose	H_2SO_4	Duration	P.ct. H_2SO_4	P.ct. Cellulose	o°C.	Hrs.	Dextrose	Acids	$[\alpha]_D$
1	5	50	3	3	0·25	120	1	113·5	5·9	+ 29·4
2	5	50	3	3	0·25	120	2	112·0	6·4	+ 40·2
3	5	50	3	3	0·25	110	1	100·4	5·1	+ 43·6
4	5	50	3	3	0·25	110	2	109·4	4·3	+ 44·8
5	2	10	1	1·2	0·2	100	5	73·4	—	
6	2	10	1	1·2	0·2	120	2	90·3	—	
7	2	10	3	1·2	0·2	100	5	94·5	—	
8	2	10	3	1·2	0·2	120	2	102·4	—	
9	2	10	24	1·2	0·2	100	5	98·7	—	
10	2	10	24	1·2	0·2	120	2	101·4	—	
11	1	10	20	2	0·2	120	1½	71·6	5·6	
12	1	10	22	2	0·2	120	1½	102·2	3·3	
13	1	10	24	2	0·2	120	1½	97·3	3·9	
14	1	10	20	2	0·2	140	1½	73·4	10·8	
15	1	10	22	2	0·2	140	1½	88·5	10·5	
16	1	10	24	2	0·2	140	1½	— 80·3	10·3	
17	1	10	24	2	0·2	120	1½	80·1	3·4	
18	1	10	48	2	0·2	120	1½	94·8	3·8	

The following investigation directly bears on the same subject :—

DIE ZERSETZUNG DER DEXTROSE DURCH VER-DÜNNTE SCHWEFELSAURE.

H. Ost and T. Brodtkorb (Chem. Ztg., 1911, 35, 1125)

(DECOMPOSITION OF DEXTROSE BY DILUTE SULPHURIC ACID)

This investigation is complementary to that of Ost and Wilkening (*ibid.* 1910, p. 46) on the problem of the total hydrolysis of cellulose. Working under the conditions of Flechsig's original investigation (1883), it is necessary to complete the hydrolysis by heating the solutions diluted to 2-3 p.ct. H_2SO_4.

The productions of organic acids always observed in the final products may be referable either to the original cellulose or to secondary reactions of decomposition determined either by the acid used in 'dissolving' the cellulose, or by the acid in its diluted state at the high temperatures adopted as giving maximum hydrolysis.

The present investigation establishes the latter as the source of the acids, and the authors conclude 'daher ist nicht mehr daran zu zweiflen dass das Cellulose-molekül sich ganz aus Dextrose-resten aufbaut'. Cellulose is as starch, a polydextrose anhydride.

As regards the experimental numbers defining the degree and direction of decomposition of dextrose under heating with dilute sulphuric acid, they are given in terms of dextrose decomposed and of the products of decomposition, formic and levulic acids and 'humus,' and cover a wide range of variations of the important factors.

Concentration of acid and dextrose, temperature of heating thus—

Dextrose in concentrations of	5·0	0·5 p.ct.
H₂SO₄	2·0	0·5 p.ct.
Temperatures of digestion .	100°	145°
Duration of digestion (hours)	1	8

The numbers obtained are important records for the general chemistry of the hexoses.

*   *   *   *   *   *   *   *   *   *

As regards cellulose, the particular or direct interest of the numbers is of course nil. Indirectly they serve to complete the demonstration of the constitutional fact (*supra*) which is of obviously capital importance.

The problem of ultimate constituent groups is, however, not finally resolved. Assuming that the carbohydrate groups retain the configuration of dextrose in the cellulose complex, it is still an open question whether the acid products of break-down represent constituent groups of the original complex or are more or less 'accidental' products of a complex resolution.

The general analogy of starch does not enable us to draw positive inferences, since the diastasic resolution of starch is free from such possible complications.

As a simplification of the reactions of resolution the acetylation of the cellulose to triacetate previously to acid hydrolysis of the complex has contributed important developments.

ACETOLYSIS.

It is suggestive of a further and more fundamental analogy of cellulose with starch that the hydrolytic resolution in both cases passes through a series of colloids of decreasing complexity terminating in a biose. We might therefore expect to be able to draw on the accepted formulation of the starch-maltose series for suggestions as to the course of cellulose resolution.

On the other hand, an examination of the extensive literature of 'starch' shows that the subject of starch transformation, by way of diastase, presents many controversial issues. Acetolysis

of cellulose and complex carbohydrates is a development of the fundamental observations of Z. H. Skraup (and collaborators) as to the course of resolution of these bodies by acids acting in presence of acetic anhydride.   Acetylation of the OH groups eliminates a complicating factor, and the final product is a crystalline acetate, at first described as the acetate of a hexose but later fully identified as a biose octoacetate (Skraup and König, 'Monatsh.,' 1901, 22, 1011; 'Berl. Ber.,' 34, 1115).   The biose is known as cellose or cellobiose, and its formation as the end term of the series of resolutions under the attack of acids, together with the conditions of reaction, justify the conclusion that starch and cellulose are constitutionally different in ultimate features as they are in proximate characteristics.

Both the biose and its acetylated derivatives have been further investigated in various directions.   E. Fischer and G Zemplen have contributed to the fuller characterisation of cellose by showing that it is hydrolysed by emulsin and not by yeast, and is probably a β glucoside.   Its osone is resolved into dextrose and dextrosone by emulsin ('Annalen.,' 1909, 365, 1).   The biose and its acetyl derivatives have been also further characterised by the researches of Bertrand and Holderer ('Compt. Rend.,' 1909, 149, 1385); Hardt-Stremayr ('Monatsh.,' 1907, 28, 63); Geinsperger ('Monatsh,' 1905, 1459); Maquenne and Goodwin ('Bull. Soc. Chim.,' 1904, 31, 854), and again by Fischer and Zemplen ('Berl. Ber.,' 1910, 2536).

More important are the investigations of the *process* of 'acetolysis' in quantitative relationships to the complex carbohydrates.   A study of the acetolysis of starch, glycogen, and cellulose (Z. H. Skraup and others, 'Monatsh.,' 1905, 26, 1415) gave the following results.   In this case the reagent was acetic anhydride saturated at low temperature with HCl :—

Starch in fourteen days was converted into a chloracetyl-erythrodextrin $(C_6H_7O_2)_6Cl . (OAc)_{17}$, which yielded erythrodex-

trin when carefully saponified. Soluble starch gave similar derivatives, and from their composition and physical characteristics it is concluded that the minimum formula for soluble starch is $(C_6H_{10}O_5)_{46-50}$.

Glycogen gives amorphous derivatives, and the results of quantitative study lead to a formula for glycogen of dimensions $(C_6H_{10}O_5)_{100}$.

Cellulose is converted in forty-eight hours' digestion into $(C_6H_7O_2)_{34}Cl$. $(OAc)_{101}$, which was saponified by alkalis to 'cellulose' $(C_6H_{10}O_5)_{34}$.

After fourteen days' digestion the main product was the hepta-acetyl-chloro cellose.

A study of the acetolysis of cellulose and derivatives by Hardt-Stremayr (Monatsh., 28, 73) established the following quantitative yields of cellobiose octoacetate (m. p. 228°) under the action of acetic anhydride and sulphuric acid: From cellulose and 'hydral-cellulose,' 25 p.ct.; from 'oxy-celluloses' (*a*) HNO_3 process, 16 p.ct., (*b*) $HCl + KClO_3$, 10 p.ct.; from 'acid-cellulose,' only 7 p.ct.

* * * * * * * * * *

On these results and discussions we make the following comments: The yields of biose are by no means such as to justify the full application of the starch-dextrine-maltose series to the case of cellulose. The intermediate terms of the cellulose . . . cellose series require further characterisation.

Acetolysis with halogen hydracids as the active agent has analogies, in regard to the attack on the actual carbon-complex of cellulose, with the break-down to ω brommethyl furfural studied by Fenton ('Chem. Soc. J., 1901, p. 361). The final condensation in this case, at the expense of OH groups, we may assume to be of the form :—

$$CH\ OH—CH\ OH \qquad\qquad CH\ \cdot\ CH$$
$$HO\cdot H_2C\ \ CH\cdot OH \quad CH\ OH\cdot CHO \quad\rightarrow\quad OH\cdot H_2C\cdot C\diagdown_O\diagup C\cdot CHO$$

(See also E. Erdmann, 'Berl. Ber.,' 1910, 2391: 'ω Oxy. symm. Methylfurfural und seine Beziehung zu Cellulose'.) A comparison of the two processes and results elucidates the actual mechanism of the simplification of the break-down of cellulose by 'acetolysis'.

But a *combination* of these processes might enable us to trace some of the intermediate steps in the condensation to furfural, and perhaps connect the furfurane O definitely with the still problematical fourth O atom of the unit group $C_6H_{10}O_5$. Further, the 'Fenton' condensation reaches a limit which is perhaps explained by the tendency of the ω Hydroxy furfural to condense with alcoholic OH groups (Cooper and Nuttall, 'Chem. Soc. J.,' 1911, 99, 1193); it is clear that the acetolysis of the residues would clear up some important quantitative relations.

The conclusions drawn from the composition of colloidal chloracetyl derivatives as to their molecular weight we need not specially criticise; it is only a particular case of the general assumption that the molecular relations of the present main fabric of the science are universally true, to the exclusion of other possibilities to account for the anomalies of colloidal matter.

As a comment we note that the comparative study of starch and cellulose by acetolysis (*supra*) shows that the latter is more reactive; and the same is true of other methods of acetylation where the complex is not resolved (*infra*).

There are, however, some general agreements on the broader features of the phenomena which we may consider :—

1. Starch is a polyhexose anhydride of complex molecular constitution and very large molecular weight. The hydrolysis through the dextrins to maltose is a graduated resolution of this complex molecule to which dimensions such as $(C_6H_{10}O_5)_{36}$ are assigned.

2. The series is dominated by exact empirical relations of opticity and cupric reduction (Fehling's solution). Opticity is

obviously a direct measure of a physical effect and condition; the chemical constant is more complex, and an indirect measure of free CO groups.

What is somewhat remarkable is the want of reference to other associated physical constants, notably solution density and viscosity, as measures of proximate state of the dextrin (colloid) . . . maltose (crystalloid) series of products. Solution densities, it is true, have been determined to a high degree of accuracy, but only as the incidental exact basis of calculation of optical and reductive constants. Viscosities, which would appear to be the only measure of the condition of colloids as such in solution, have been left out of consideration.

In regard to *solution densities* we have dealt with some features of those in a communication in ' Berl. Ber.,' 42, 2198 (1909), which we reproduce as follows :—

DAS MOLEKULAR-UND DAS LÖSUNGS-VOLUMEN VON COLLOIDALEN KOHLENHYDRATEN.

The current conception of ' starch ' as a chemical individual is that of a molecule of large dimensions, and this has been applied by analogy to cellulose. It is an integral expression of the ' constants ' obtained for the series of hydrolytic transformation products.

The alternative view of both starch and cellulose is that the state of matter in these complexes is conditioned by a differentiation affecting the ultimate constituent groups which are not *free molecules* of the configuration of dextrose (or maltose), but units which have a particular mutual relation causing association into complexes; these complexes are reacting units in the sense that any change impressed upon any constituent group affects the whole complex. No dimensions can be assigned to these complexes, as there are no physical terms of measurement which can be applied. There is evidence that reactions both in starch and cellulose are virtually continuous. At the same time, in the case of starch, it is

established—though the fact is often overlooked—that maltose appears in the earliest stage of its hydrolytic transformation. This is less consistent with the conception of a 'large molecule' and its resolution, which would be rather pictured as following the course of graduated proximate divisions—with the ultimate products appearing later in the series. It is more consistent with views such as we have indicated in general terms in our previous work.

For the elucidation of problems of such extraordinary complexity as the constitution of starch and cellulose new physical methods are evidently necessary, and especially such as measure quantities which are molecular, or at least in ascertainable relationship to the reacting unit.

Of possible methods, those dealing with the constants of volume—specific volume—must have a fundamental relation to the proximate or reacting complex, as to the ultimate component groups of assumed dimensions $C_6H_{10}O_5$.

Although many of the typical reactions of starch and cellulose, especially those of synthesis, can be formulated by means of the simple unit, it is usual to regard these compounds as polymolecules of large dimensions. This view is actually an integration of the quantitative results of their hydrolytic resolution, which in the case of starch takes the course of the extremely complex series, soluble starch, dextrins, maltose, etc. In confirmation of such formulæ, e.g. $(C_6H_{10}O_5)_{36}$, the results of physical measurements, such as osmotic pressure, vapour tension, freezing-point of solutions, have been applied generally to the soluble intermediate colloidal products without critical inquiry as to whether the colloidal state does not introduce a disturbing factor.

We suggest some considerations, based on specific volumes and the methods of J. Traube, which have been formulated in a series of communications on molecular volumes and molecular solution volumes.

The relationships which he has developed are in the main on a purely empirical basis; but in applying the methods to a very large range of molecular compounds, his conclusions are found to present a very general coincidence with other molecular constants, and contain therefore the germs of a progressive realisation of factors of volume not yet clearly dissected from the complex phenomena.

Applying these methods, for instance, to starch, solid dry starch may be taken to have the density of 1.654 and therefore gram molecular volume of 98.5. Soluble starch has been very carefully studied by Brown, Morris, and Millar as the basis of exhaustive work on the hydrolysis of starch ('Chem. Soc. J.,' 71, 1997; 72, 193).

From their numbers we have a value of 92.6-93.3 as the molecular solution volume of soluble starch, and applying Traube's formula and constants, and calculating molecular solution volume for the unit in which we assume that of the five oxygen atoms, three are as OH groups, one as CO, and the fifth presumed as of ethereal type we have the following relations :—

$$
\begin{array}{lllllllr}
C_6 & . & . & . & . & . & . & . & 59.4 \\
H_{10} & . & . & . & . & . & . & . & 31.0 \\
O_3(OH) & . & . & . & . & . & . & 1.2 \\
O(CO) & . & . & . & . & . & . & 5.5 \\
O(-O-) & . & . & . & . & . & . & 5.5 \\
\hline
& & & & & & & & 102.6
\end{array}
$$

To these numbers we add the constant for co-volume, namely 12.4, giving the number 115, which shows a large divergence from the volume actually observed.

It is this point which appears to have been overlooked, and which requires critical examination. In considering the solution volume of monoses and bioses, more particularly those which contain aldehydic CO groups, Traube has already shown that the divergencies are of such magnitude as to be inconsistent with the aldehyde formula, indicating that in such sub-

stances the aldehyde group takes the hydrated form, $CH(OH)_2$, and consequently the oxygen volume is reduced in terms of $5.5 - 2 \times 0.4 = 4.7$.

And even if we take his extreme hypothesis, the number 0.4 for the whole of the five oxygen atoms, the sum of the volumes of constituents would only be 111, and this is still a very large divergence from the mean of 93 which represents the actual experimental determination of volume.

If we assume that solid starch is a homogeneous substance in the sense of Traube's discussion, its molecular volume of 98.2 is a very striking divergence from the general relationships.

In such cases the general formula for calculated volume is

$$\frac{\Sigma nC + 12.4 + 13.5}{A}$$

in which A is an association factor, which would further increase the number 111, calculated as the minimum for the molecular solution volume of 'soluble' starch.

The calculated numbers for a series of carbohydrates according to Traube we have below :—

				Obs	Calc. for $\Sigma nC + 12.4$
Pentoses					
Xylose	.	.	.	96.4 ⎫	100 0
Arabinose		.	.	93.2 ⎭	
Hexoses					
Dextrose		.	.	112.0 ⎫	
Levulose		.	.	111.0 ⎬	116.5
Galactose			.	110.0 ⎭	
Bioses					
Cane sugar		.	.	210.0 ⎫	
Milk sugar		.	.	205.0 ⎬ 208.9	
Maltose	.	.	.	205.0 ⎭	
Cycloses					
Quereite	.	.	.	105.5 ⎫ 111.0	
Inosite	.	.	.	99.5 ⎭ 111.4	

In this series the difference between observed and calculated volume is greater than 1-2 units, which represents the extreme variation for most of the cases investigated.

The carbohydrates in the above table, with the exception of cane sugar, have a smaller volume than calculated.

In the case of the monoses this can be explained as stated by regarding the carbonyl CO group as taking the alternative form in solution, viz. $CH(OH)_2$.

In the case of cycloses, the configuration of the carbon ring affords a further explanation. Traube shows in the case of benzene, naphthalene, anthracene, and hexamethylene that the cyclic constitution causes a decrease of 8·1 for each ring. The furfural ring gives a decrease in volume of 6·8. Applying these considerations to starch, it may be assumed that this substance passing into solution as 'soluble starch' is changed by extensive ring formation; and this may also hold good for solid starch.

This suggestion we do not propose to discuss in detail, but to propose it as a working hypothesis for critical investigation.

In the case of cellulose, the matter is complicated by a much greater experimental difficulty in determining the solution volume. We may assume that the amorphous structureless forms of cellulose obtained from solutions are closely representative of the actual condition of cellulose matter in solution, and we find that the density dimensions give very similar numbers to those in the case of starch. The numbers are much less than for a polymerised dextrose or hexose anhydride. In previous communications we have suggested a cyclic C_6 formula for the reacting unit, and the grouping C_6—C_6 as consistent with many critical facts of cellulose chemistry; this would also be consistent with the anomalous density.

In the investigations on cotton and denitrated cotton, H. de Mosenthal supplies some numbers which confirm this view.

Thus, for the nitrates we find that in acetone solution the dinitrate loses 8·1 c.c. per gram molecule, and for a nitrate with 13·2 p.ct. nitrogen, 10·2 c.c. per gram molecule.

In this series we also find that the nitro groups successively

introduced have a constant molecular volume, namely 26·8 c.c., whereas for simpler alcoholic nitrates, such as glycerine, there is a decrease of volume of the nitro groups from the first to the third combining.

This point, together with the variations in solubility, may find some explanation of the hypothesis of cyclic groups opening and closing under varying conditions of reaction.

The experimental numbers in De Mosenthal's communication are not sufficiently numerous to enable us to draw positive conclusions. but they indicate a useful direction of investigation. Such investigations we propose to undertake.

Professor Traube adds the following critical remarks in reference to the foregoing :—

The atomic volumes and co-volumes have been determined by two methods : (1) By the method of Kopp, comparing molecular volumes and molecular solution volumes of homologous or otherwise closely related compounds.

(2) By the help of the equation of Van der Waals. I have calculated the atomic volumes (b) from observed volumes at two temperatures, and from these have obtained the value for v-b or co-volume.

Cross and Bevan have applied the former method, which leads to the conclusion that the co-volumes in aqueous solution are constant, whereas, according to the latter, these are dependent upon the cohesion pressure of the substance.   I therefore suggest that the former method, applied by Cross and Bevan, is purely empirical in value, but this does not lessen the probable value of its application in solving constitutional points, as in my previous communications has frequently been shown.

I entirely concur with the opinion of Cross and Bevan that the smaller volumes of soluble starch and cellulose are very striking, and, further, are best explained by the hypothesis of cyclic structure.

I am also entirely of their view that the molecules of

soluble starch and cellulose are of very much less dimensions than those generally assumed.

The determination of molecular weight, and dimensions on the basis of osmotic pressures, I hold to be of no value whatever in the case of colloids.

We conclude this chapter with a notice of a research on :—

SOME NEW SOLVENTS FOR CELLULOSE AND THEIR ACTION ON THIS SUBSTANCE.

H. G. DEMING ('J. Amer. C. S.,' 33, 1515, 1911).

The author has studied the action upon cellulose of solutions of various salts in concentrated halogen acids. Solutions of mercuric, bismuth, and stannous chlorides in hydrochloric acid act rapidly ; chlorides of cobalt, gold, uranium, cerium, and chromium are less active.

A large number of qualitative observations of this order are recorded. The cellulosic products recovered from these solutions by dilution are examined ; the insoluble products are 'modified celluloses' with considerable action upon Fehling's solution.

It is noted that soluble intermediate products of the dextrin type are conspicuously absent.

In a section headed 'Esterification and Hydrolysis in Formic Acid Solution,' observations are recorded of interaction of cellulose and formic acid in presence of hydrochloric acid and calcium chloride.

The author notes that esterification takes place, but is followed by hydrolysis of the ester ; consequently the insoluble products from such reactions are found to be colloids of the composition of cellulose, which he also terms 'modified celluloses'.

The author sums up his observations in a concluding section which we reproduce in full :—

Cross and Bevan have attempted to explain the solution of cellulose in the zinc chloride reagent by stating that the process is analogous to that involved in the formation of double salts. Nevertheless no such compound has even been isolated.

The assumed 'amphoteric' character of the cellulose molecule is still unproven, since it has its chief support in facts which may find an explanation as capillary phenomena. The idea has also been advanced that such solutions are due to the formation of alcoholates, but this theory is hardly admissible, since such compounds would be broken down by the strong acids employed.

The most probable explanation for this class of cellulose solvents is, accordingly, the one first presented, which seeks to connect the process of solution in the reagents discussed, with the phenomena of hydration and adsorption in the presence of certain salts.

It has been shown that cellulose in the form of filter paper is soluble in concentrated aqueous solutions of certain salts, such as antimony trichloride, stannous chloride, and zinc bromide.

In solution in the aqueous hydrohalogen acids these salts and many others dissolve cellulose with extreme ease, as do also a few salts in formic acid and trichloracetic acid.

The solution of cellulose in these reagents is connected with facts previously known in a manner which may be summarised as follows :—

Cellulose attracts metallic salts in solution to an extent depending upon its mechanical structure and degree of hydration, on the nature and concentration of the salt, and on the temperature. This attractive force is opposed by that existing between the salt and its solvent; hence the final result is a distribution of the salt between the fibre and the solution.

In concentrated solutions the attraction between the absorption complex and the solvent may manifest itself in one of two ways, viz. either the complex becomes hydrated, or else the reciprocal attraction of the solvent for the complex may bring the latter into solution. The latter effect obtains only where a

high temperature is employed, or where some agent is present which, like certain dilute acids, can bring about a union with water.

In support of the above view, it has been shown that cellulose modified by acids becomes soluble in certain reagents, such as an aqueous solution of calcium chloride, which are unable to dissolve cellulose not so modified.

Chlorosulfonic acid, arsenic, and selenic acid have been shown for the first time to possess the power of dissolving cellulose.

Celluloses dissolved in the acid solutions of the salts studied may be precipitated as amorphous compounds, distinguished from the original material by their marked reducing qualities and ease of hydrolysis. These substances have been described simply as modified celluloses, until their relation to each other and to the so-called hydro- and hydra-cellulose can be determined.

One of the formates of cellulose has been studied with regard to the type of cellulose produced by its saponification by the agency of concentrated hydrochloric acid. Further action of this material converts the cellulose into water-soluble products, and finally into glucose, but no evidence is at hand to show that the production of this sugar can be made quantitative.

The writer desires to reserve for a future paper the study of the reducing power, dyeing capacity, and hydrolysis of the cellulose precipitable from the reagents presented, in order to determine their relations to each other, to various other modified celluloses, and to the parent substance. A further study of the process of hydrolysis will be made to ascertain what substances are present in the final stage where glucose is produced. It is hoped that some of the reagents discussed may prove useful in separating and studying various modified celluloses.

*   *   *   *   *   *   *   *   *   *

Upon this communication we submit the following comments :—

The reactions investigated are not characteristic as solution reactions of cellulose in the same sense as are the solutions in zinc chloride on the one hand, and cuprammonium on the other.

The quantitative recovery of ' cellulose ' from these solutions without change of characteristic physical properties, or of reactions, especially such as mark the absence of free CO groups, is evidence that the effects are in the main hydration effects.

In these typical cases, moreover, definite compounds of cellulose and the metallic oxide (hydrate) are isolated by special methods of precipitation, which negatives a prominent statement of the author's in criticism of the simple explanation of these solution reactions We prefer to regard them as double interactions of acid and basic groups of metallic compounds on the one hand, and cellulose on the other, the cellulose representing a colloidal complex of reacting groups in amphoteric equilibrium.

In the case of zinc chloride there is no complicating factor. In the cuprammonium solution the ammonia may react with CO groups of the cellulose, and the cupric oxide might have a catalytic action of oxidation and reduction within the complex, causing changes of configuration but without final disturbance of the oxygen equilibrium.

In both cases, however, there is a definite combination of the cellulose (hydrate) with the metallic hydroxide.

But we may further point out that the view of cellulose as a typical amphoteric complex rests on a wider basis. There is not only the evidence of electric conductivity of the electrolytic order, but the general collateral evidence of the dependence of the colloidal state upon polar or electric energy affecting on the one hand the interior equilibrium of its constituent groups, and on the other the relationship of these groups to the fluid medium in which the more special properties of the colloid become active (' Researches on Cellulose,' II., 1905).

The special cases investigated by the author appear to depend primarily upon the attack of acids of high avidity,

modified and restrained from dehydration and condensing actions by the presence of the basic oxides. They are solvent actions on an obviously lower plane, that is, with an initial degradation of the colloid.

The cases involving the joint action of formic acid are complicated by the peculiar relationships of this acid to cellulose. The author's results are in confirmation of our own described on p. 86. The formic esters appear to exist in unstable forms, and revert to 'modified celluloses' under conditions which would not affect normal esters of other monohydric acids by nitrates and acetates.

CHAPTER III

CELLULOSE ESTERS

Various sectional contributions are noticed in the following order :

Acetolysis, the results of a more special study of cellulose and starch (Schliemann).

Acetates of starch and cellulose and the acetylating process in relation to the action of catalysts (J. Gutsche).

Formyl derivatives of cellulose, and a study of its interaction with formic acid (the authors).

Xanthogenic esters of starch and cellulose by H. Ost, Westhoff, and Gessner, and by the authors with J. F. Briggs.

CELLULOSE AND ESTER-REACTIONS.

Investigators in this field have devoted themselves mainly to the acetates and the xanthic esters (viscose), the former being true ester anhydrides, sensitive to alkalis, which rapidly saponify them, the latter are produced by reactions in which alkalis and water play a determining part. Thus 'viscose' may be regarded as a form of cellulose representing the maximum of hydration. Reactions of cellulose with formic acid have been studied, and a number of new derivatives of this group have been described.

In regard to the general relationships of the acetates, it is obvious that they also involve the question of the normal series, since acetylation is a process with collateral actions and effects which modify the parent complex more or less. In the earlier researches (of Schützenberger and Naudin, Franchimont and others, to 1892) this point was not considered.

When we resumed the study of these derivatives we became aware of these complicating effects and that these may ensue after the point of maximum normal acetylation is passed ; this separation of effect is of course only possible in a process which is graduated and controlled, and fulfils more or less the definition of a 'normal process'. We may treat this case similarly to that of 'cellulose' (p. 18).

The 'normal process of acetylation' is a progressive esterification in which the structure of the fibrous celluloses is maintained and the yields of ester are quantitative ; the product is a normal acetate from its structural or physical characteristics, and from the fact of reversion on saponification to a cellulose of normal characteristics.

This degree of control and the definition of the result is a main result of continued study of these derivatives. As regards the maximum acetylation it was always suggested from the sufficiently close analogy of the nitrates, that the triacetate (C_6) would represent a limit of acetylation of the normal cellulose. But the unit group $C_6H_{10}O_5$, with $3OH$ groups as such, has further potential modes of acetylation ; the aldehydic (or ketonic) CO could combine, and the fifth O atom, either representing an ether linking, or tertiary alcoholic OH, or even combined in a heterocyclic group. In both directions it is clear that the oxygen affinities may be concerned in the constitution of the aggregate, and therefore that acetylation at these points would involve constitutional changes, and therefore also probably structural modifications.

The question involved, therefore, in the problem of a higher acetate is the fundamental one of constitution and structure. It is remarkable, as we have often pointed out, that a trinitrate and triacetate may be formed with the minimum of structural modification ; in other words that the OH groups do not directly affect the constitution of the complex ; and from another point of view that new matter can be introduced into

a colloidal system increasing its mass by 75 p.ct., and producing only slight modification of the characteristics of the colloid. This striking fact has not, we think, received the attention it deserves as a prominent phenomenon affecting our conceptions of colloidal matter.

In our investigations which led us to formulate a tetracetate, we were dealing not with the normal cellulose but with the cellulose modified by reaction with alkali (mercerisation) and carbon bisulphide (viscose). The essential modification is a change of function and position of the CO group.   As *under the action of* acids the changes are towards aldehydic function and position, with ultimate production of dextrose, under alkalis the CO group loses reactivity, and with associated changes of density we may infer that the change is towards ketonic constitution or cyclic configuration.   In this case, therefore, any higher degree of acetylation—above the triacetate —may be inferred to occur at the position occupied by the fifth oxygen.   This was the order of reasoning to account for the higher degrees of acetylation which we certainly observed. Our critics, who have decided that the tetracetate does not exist, appear to regard the point as merely one of quantitative analytical method, and of errors of method on our part.   And they attach no significance to the question of constitution of the cellulose taken as the basis of investigation.   We shall revert to this point after reviewing the publications cited above.

On the question of method, our records (1892-95) of researches show a general application of methods of both alkaline and acid (H_2SO_4) saponification, and verifications by distillation and re-distillation of the actual volatile acid.

We also applied a special method which we now bring into notice, as it may be found to give results of critical importance.

After solution in H_2SO_4 we oxidised with CrO_3 by our

method of ultimate combustion ('Chem. S. J.,' 53, 889). The following numbers are from our records of 1894, and show that the combustion is mainly of the cellulose complex, and that the acetyl groups are unaffected :—

Combustion of cellulose acetate by CrO_3 after solution in H_2SO_4 percentages of carbon calculated from gas volume obtained :—

Preparation	(a)	(b)		(c)	
	25·3	26·3	24·9	24·6	24·6

These numbers are uncorrected and therefore somewhat lower than the 'theoretical'. For the cellulose carbon in a triacetate the theoretical number is 25·0. The numbers, however, are only approximate, and appeared to indicate that the combustion was not quantitatively limited to the carbon of the cellulose complex. This method may prove of value not only in the analysis of these acetic esters, but in investigating complex products of the cellulose group, e.g. ligno-celluloses, in which acetic residues exist in combination (p. 101). Throughout our researches in fact we had always in mind a possible contribution of acid from the cellulose itself as a product of break-down under saponification. From the results of our investigations of formic esters and derivatives, this probability is confirmed.

It is also possible that as there are unstable conditions of formic residues in combination with cellulose, so also a higher acetate, if formed, may represent a less stable combination of acetyl groups in excess of the three.

This preliminary exposé will enable the reader to follow critically the following brief analytical résumé of the more important publications.

CELLOBIOSE UND DIE ACETOLYSE DER CELLU-LOSE.

W. SCHLIEMANN (Annalen, 378, 366).

[An investigation carried out in the laboratory of Professor H. Ost, Hannover, published in fuller detail in author's 'Dissertation,' 1910.]

In view of the critical importance of cellose or cellobiose in relation to the sugars, and more particularly to constitutional problems in the cellulose group, the author has carefully determined its constants.

Preparation.—Either by the method of Skraup and König, or Maquenne and Goodwin, cellulose fails to yield more than 20 p.ct. of the fully acetylated product. After alkaline saponification the resulting biose requires to be recrystallised several times to eliminate saline impurities, this reduces the actual yield to 50 p.ct. of the calculated. The pure product dried at 100° has the composition $C_{12}H_{22}O_{11}$.

The *rotation* of the biose is constant for solutions of 2-17 p.ct. concentration.

The mean constant is $[a]^{20}_D = + 34^{\cdot}6$.

. In regard to solution density the values closely agree with those for sucrose.

Cupric Reduction.—The constants with Fehling's solution compared with maltose are for cellobiose 1·43-1·52, for maltose 1·13-1·17.

Osazone.—The melting-point when rapidly heated is 208-210°. In solution in absolute alcohol the rotation is $[a]_D = - 17^{\cdot}5$.

The Isomeric Octoacetates.—The two isomerides have the following characteristics :—

	(1)	(2)
melting-point	222°	192
$[a]_D$	+ 41°·5	− 7°·5

As regards their relative production and equilibrium under varying conditions of treatment, the following tabular summary of results of investigation clears up some conflicting statements of previous investigators.

Substance	Treated with acetic anhydride in presence of		
	Sulphuric Acid	Zinc Chloride	Sodium Acetate
	(a)	(b)	(c)
Cellobiose . . .	$[a]_D + 33\cdot4$	$+ 29^\circ\cdot4$	$- 4\cdot3$ to $- 5\cdot0$
Acetate $[a]_D = + 41\cdot5$.	$+ 33\cdot1$	$+ 30^\circ\cdot3$	$+ 41^\circ\cdot7$ .. $+ 42\cdot0$
Acetate $[a]_D = - 7^\circ\cdot5$.	$+ 35\cdot0$	$+ 30^\circ\cdot6$	$- 7\cdot8$., $- 8\cdot6$

The products are mixtures containing in the several series : (a) 84 p.ct., (b) 77 p.ct., (c) 6 p.ct., of the acetate of $[a]_D$ $41^\circ\cdot5$.

The isomerides may be separated (fractionated) on the basis of relative solubilities in benzene and alcohol.

Acetolysis of Cellulose.—In view of the special importance of this section we reproduce it in fuller detail.

In applying the reactions of acetic anhydride with cellulose in presence of catalysts (H_2SO_4 or $ZnCl_2$) in sufficient proportion to resolve the complex, it is found that the crystalline cellobiose acetate is accompanied by a series of amorphous (colloidal) intermediate products which have been partly investigated by Franchimont ('Berl. Ber.' 12, 1941, 1879 ; 14, 1290, 1881 ; 'Rec. Trav. Chim.' 18, 472, 1879), Skraup ('Berl. Ber.' 32, 2413, 1899), and V. Hardt-Stremayr ('Monatsh.,' 28, 65, 1907).

Those derivatives being acetates probably of hydrolysed celluloses, they may be referred to formulæ analogous to that adopted by Ost for the higher acetates, the ordinary triacetate, viz. $(C_6H_{10}O_5)_6H_2O$ with 6×3 acetyl groups. The author suggests, however, that each H_2O fixed should represent two OH groups, i.e. two additional OAc groups in the acetate. Therefore

that the acetate of a unit $(C_6H_{10}O_5)_6H_2O$ contains 20 OAc groups $= 65.6$ p.ct acetic acid on hydrolysis.

The questions involved in relation to the series are primarily to be resolved in terms of percentage of OAc groups. The method of acid (H_2SO_4) saponification, followed by dilution and distillation is subject to an error due to the formation of other volatile acids, which increase with concentration of the acid. To eliminate this acid from the result, the distillation is carried out at constant volume and continued for four hours ; the acetic acid is quantitatively distilled in this period of time. The distillation is continued for a second period of four hours, and, it is assumed, with an equal production of other volatile acids at the expense of the cellulose or other residues. The corresponding acidity is deducted from that of the distillate of the first period.

In the case of cellobiose acetate (pure) the following figures were obtained :—

	1st Period	2nd Period	Difference or true percentage
Acetic acid . .	72·3	0·8	71·5
	77·3	5·5	71·8

The error of the method with this correction is $\pm$ 1 p.ct. acetic acid.

The following results are recorded :—

1. Normal cellulose acetates (process of D.R.P. 159, 524) were found to yield 54·3 – 60·9 p.ct. acetic acid. The sp. rotation of these acetates in solution varied from $- 18°$ – $14°$ $[a]_D$.

2. Cellulose treated with acetic anhydride and zinc chloride gave a series of acetates. The last fraction insoluble in alcohol, soluble in chloroform, gave acetic acid 62·8 and $[a]_D = - 11°$. The fractions soluble in alcohol were found to contain a product less soluble than the cellobiose acetate giving acetic acid 63·4 p.ct. and $[a]_D = - 10°$ and also a fraction much more

soluble with 65 p.ct. acetic acid, the composition of which was not affected by several recrystallisations.

3. In normal acetylating conditions prescribed by Maquenne and Goodwin, limiting the temperature to 90°, or reducing the proportion of H_2SO_4 to a minimum, acetates were obtained, very soluble in alcohol, giving acetic acid $66\cdot3 - 67\cdot3$ p.ct. and $[\alpha]_D + 11°\cdot5 - + 18°$ and from the mother liquors from these, benzene-soluble acetates with $68\cdot5$ acetic acid and $[\alpha]_D + 18°$.

4. On treating alcoholic mother liquors from normal acetylations, acetates are precipitated with $70\cdot5$ acetic acid and $+ 18°$ $[\alpha]_D$.

5. The α cellobiose acetate with $70\cdot8$ p.ct. acetic acid and $+ 41°\cdot5 \; [\alpha]_D$ appears therefore to stand at the end of a series characterised by increase of specific rotation *pari passu* with increased proportion of acetylation.

The products described under (3) confirm the author's view of derivation from a 'hydrocellulose' or 'cellulose dextrin' $(C_6H_{10}O_5)_4 \cdot H_2O$ with $14 \cdot OH$ groups. It appears also from the results under (4) that other bioses result from the acetolysis of cellulose.

ACETYLATION OF CELLULOSE AS A TREATMENT OF COTTON TO RESIST DIRECT COLOURS IN DYEING.

C. F. Cross and J. F. Briggs ('J. Soc. Dyers and Colourists,' 1908, 24).

1. The purpose of this investigation was to acetylate without the obvious risk, always present in methods which employ acid catalysts, of attacking the cellulose complex itself, and in their limiting reaction, to obtain the normal series of derivatives with the physical properties and therefore textile characteristics of the fibre fully preserved. The attendant

result or effect of modifying the dyeing capacity is from our present point of view of secondary interest. The conditions of acetylation for this normal series are with the usual reagents acetic anhydride and glacial acetic acid in equal proportions, zinc chloride as catalyst, but employed in much increased proportion, 6-10 p.ct. of the mixture, and a range of low temperatures.

Under these conditions the control of the process is complete—any desired degree of acetylation of the cotton can be attained, and even with minimum proportions of acetylating mixture to cellulose the effective utilisation of the anhydride reaches 80 p.ct. of the theoretical. The treatment consequently fulfils the requirements of an economical industrial process.

Observation of the course of reaction shows that up to the monoacetate the fibrous celluloses preserve their minute structural features unchanged; as the stage of diacetate is reached the fibres swell and become transparent: these changes are much exaggerated at the stage of combination with $2\frac{1}{2}$ molecular proportions of acetyl: at and from this point the acetates pass into solution in the mixture to a solution of maximum viscosity.

ZUR KENNTNISS KATALYTISCHER WIRKUNGEN BEI DER ACETYLIERUNG VON STÄRKE UND CELLULOSE MIT ESSIGSÄUREANHYDRID.

J. Gutsche ('Diss.' Heidelberg, 1910).

This investigation is in the main a study of the acetylation of starch and cellulose, by the agency of acetic anhydride, with particular reference to the function of catalysts in determining reaction. We may characterise it as exhaustive of the particular points of method and results, and trustworthy in general conclusions. As catalysts, sodium acetate, zinc chloride, and sulphuric acid have been employed by previous investiga-

tors under varying conditions (Liebermann, Franchimont, Skraup, Lederer). The author has studied comparatively the actions of the following : Copper sulphate ($CuSO_4 . H_2O$), ferrous sulphate ($FeSO_4 . H_2O$), sodium phosphate ($HNa_2 . PO_4$), hydrogen potassium sulphate ($HKSO_4$), ammonium persulphate [$(NH_4)_2S_2O_8$], stannous chloride ($SnCl_2 . 2H_2O$), trichloracetic acid ($CCl_3 . COOH$), methylamine sulphate ($CH_3NH_2)_2 . H_2SO_4$, and pyridine sulphates ($C_5H_5N)_2H_2SO_4$.

The forms of starch and cellulose taken were a 'pure' potato starch and a 'pure' bleached cotton (Verbandwatte), and the investigations cover over 800 quantitative operations, involving determinations of yield, composition (percentage acetyl), solubilities (in water, chloroform, acetic ether, acetone, and acetic acid), viscosities of solutions, cupric reduction (Fehling's solution).

The general conditions of the acetylation treatment were :—

5·00 grms.	Substance (dry)	⎫	at temperatures
20·00 ,,	Acetic acid (glacial)	⎱	60°, 80°, 100°
25·00 ,,	Acetic anhydride	⎰	and times 5 to
0·50 ,,	Catalyst	⎭	200 hours.

The quantitative results comprise the following determinations :—

1. Yield of acetylated compound.

2. Composition : percentage acetyl by alkaline saponification (Gutsche), and, in the cellulose derivatives, viscosities of solutions.

3. Reduction of cupric oxide (Fehling's solution) ; observed in extreme products and an index and measure of the hydrolysis of the cellulose complex.

In regard to the quantitative methods adopted—

1. The yields are those of crude precipitated and washed products.

2. The methods proposed by Perkin ('Chem. Soc. J.,' 89, 811) and Ost ('Ztschr. angew. Chem.,' 1906, 1993) gave satisfactory results with the starch derivatives, and concordant with

5 *

STARCH.

Percentage of Acetyl.

Time	Without Catalyst	CuSO₄ + OH₂	CCl₃COOH	(CH₃NH₂)H₂SO₄	HKSO₄	FeSO₄ H₂O	HNa₂PO₄
						Acetylating Temperature 85°C.	
9	4·0	17·1	—	17·3	—	—	—
26	—	39·0	13·9	41·6	—	—	—
50	10·7	42·2	21·2	13·3	—	—	—
100	11·2	45·4	34·0	16·6	—	—	—
200	17·6	46·1	42·5	52·2	—	—	—
						Acetylating Temperature 100°C.	
2	—	—	7·0	38·7, 39·6	—	—	2·5
5	11·2, 11·9	32·9	11·9	13·4, 13·8	18·0	23·2	6·1
12	13·7	43·9	29·1	18·6, 46·2	23·5	34·9	13·3
26	24·3, 23·8	44·5, 43·9	35·6	—	39·4	13·9	19·7
50	32·7	45·2	40·5		10·9	45·5	35·6
100	43·1	45·5	45·8		46·0, 46·5	45·0	42·6
200	44·4, 45·2	45·7	46·6, 46·0		45·0, 46·0	45·7	44·7, 44·8

YIELD.

FROM 5 GR. DRY STARCH.

Time	Without Catalyst	CuSO₄ . H₂O	CCl₃COOH	(CH₃NH₂)₂H₂SO₄	HKSO₄	FeSO₄ . H₂O	HNa₂PO₄
Acetylating Temperature 80°C.							
9 . . .	5·0	5·4	5·9	5·4	—	—	—
26 . . .	5·0	7·2	5·5	7·8	—	—	—
50 . . .	5·2	8·1	5·7	7·7	—	—	—
100 . . .	5·4	7·6	7·5	7·0	—	—	—
200 . . .	5·7	7·7	8·4	6·2	—	—	—
Acetylating Temperature 100°C.							
2 . . .	—	—	5·0	—	5·3	—	5·0
5 . . .	5·3	6·4	5·4	7·1	5·4	6·0	5·3
12 . . .	5·4	7·2	6·4	6·2	6·0	7·3	5·6
26 . . .	7·0	7·2	7·0	3·8	7·1	7·6	6·0
50 . . .	7·4	7·5	7·8	—	8·0	7·7	7·5
100 . . .	7·9	6·3	8·3	—	6·3	7·6	8·5
200 . . .	8·0	7·8	7·8	—	8·2	7·8	8·6

CELLULOSE.

PERCENTAGE OF ACETYL.

Time	Without Catalyst	$CuSO_4 . H_2O$	CCl_3COOH	$(CH_3NH_3)H_2SO_4$	$HKSO_4$	$SnCl_2 . 2H_2O$	$(NH_4)_2S_2O_8$
					Acetylating Temperature 60°C.		
1	—	12.2	—	—	—	—	—
2	—	28.2	—	—	—	—	—
4	—	—	—	10.3	—	—	—
8	—	43.8	—	35.0	—	—	—
10	—	—	—	44.1	—	—	—
26	—	45.5	—	45.2	—	—	—
50	—	45.3	—	45.2	—	—	42.3
100	—	45.7	—	46.1	—	—	46.5
200	45.5	—	—	—	15.3	—	
					Acetylating Temperature 80°C.		
9	10.0	46.9, 46.7	14.2, 16.0	46.6	14.5	36.5	44.5
26	24.7	46.5, 47.2	27.0, 27.0	48.9, 49.5	38.2	41.0	46.6
50	46.5	47.3, 47.1	43.5	49.1	39.6	41.2, 45.8	46.6
100	46.3	46.8	47.1, 46.9	57.7, 56.9	44.6, 44.8	45.4, 45.6	55.5
200	46.7	47.0, 47.1	46.7	66.81	46.3, 45.3	45.7, 45.4	55.4
300	—	—	—	65.81	—	—	—

YIELD.

FROM 5·0 GR. DRY CELLULOSE.

Time	Without Catalyst	CuSO$_4$, H$_2$O	CCl$_3$COOH	(CH$_3$NH$_3$)$_2$H$_2$SO$_4$	HKSO$_4$	SnCl$_2$. 2H$_2$O	(NH$_4$)$_2$S$_2$O$_8$
					Acetylating Temperature 80°C.		
9 . . .	5·2	8·9	5·8	8·9	5·8	7·5	8·4
26 . . .	6·2	8·7	6·8	8·8	8·7	8·1	8·2
50 . . .	8·7	8·9	8·8	8·8	8·9	9·0	8·2
100 . . .	8·8	8·8	8·8	8·0	9·0	8·9	7·7
200 . . .	8·7	8·9	8·9	7·7	9·0	8·6	6·8
300 . . .	—	—	—	6·9	—	—	—

FEHLING'S SOLUTION.

P.CT. Cu ± 0·5 P.CT.

Time	Without Catalyst	CuSO₄.H₂O	CCl₃COOH	(CH₃NH₃)₂I₄SO₄	IIKSO₄	SnCl₂.2H₂O	(NH₄)₂S₂O₈
					Acetylating Temperature 60°C.		
1	—	Slight reduction	—	—	—	—	—
2	—	5·0	—		—	—	—
4	—	—	—	Slight reduction	—	—	—
8	—	4·9	—	3·7	—	—	—
10	—	—	—	3·6	—	—	—
26	—	5·0	—	4·4	—	—	*6·2
50	—	*5·9	—	*6·2	—	—	*5·9
100	—	*6·1	—	*6·1	—	—	—
200	No reduction	—	—	—	No reduction	—	—
					Acetylating Temperature 80°C.		
9	No reduction	*5·9	No reduction	7·1	3·0	No reduction	5·6
26	,,	*5·8	,, ,,	*12·5	*6·2	,,	8·7
50		*6·3	Slight	*12·6	*5·9	3·8	10·5
100	4·4	*6·3	4·9	*12·9	*6·7	7·7	34·9
200	4·7	*13·2	7·6	31·6	7·6	8·8	54·7
300	*6·3	—	—	5·7	—	—	—

CELLULOSE.

RELATIVE VISCOSITY 17°C.

Time	Without Catalyst	CuSO₄·H₂O	CCl₃COOH	(CH₃NH₂)₂H₂SO₄	HKSO₄	SnCl₂ 2H₂O	(NH₄)₂S₂O₈
					Acetylating Temperature 80°C.		
9 . . .	Insoluble	1·402	Insoluble	1·371	Insoluble	Insoluble	1·468
26 . . .	,,	1·325	,,	0·454	Imperfect solution	,,	0·511
50 . . .	1·586	0·872	Imperfect solution	0·192	1·345	1·445	0·213
100 . . .	1·383	1·516	1·575	0·097	1·552	0·688	0·071
200 . . .	1·638	0·366	1·799	0·075	1·535	0·678	0·070
300 . . .	—	—	—	0·071	—	—	—
					Acetylating Temperature 60°C.		
8 . . .	—	1·716	—	—	—	—	—
10 . . .	—	—	—	1·682	—	—	—
26 . . .	—	1·472	—	1·444	—	—	—
50 . . .	—	1·454	—	1·763	—	—	1·534
100 . . .	—	0·986	—	1·151	—	—	1·075
200 . . .	Imperfect solution	—	—	—	Imperfect solution	—	—

the results of alkaline saponification.   With the cellulose acetates, on the other hand, the method of Perkin was found to be inaccurate ("zu ungenau").   Ost's method of solution in H_2SO_4 and diluting and distilling after forty-eight hours, was found unsatisfactory, the author noting the much greater resistance to the acid saponification of the cellulose by comparison with the starch acetates.

The following numbers are comparative results which we reproduce in view of the importance which has been attached to the analytical estimation of the degree of acetylation :—

Saponification H_2SO_4 in presence of alcohol (Perkin)	Saponification H_2SO_4 steam distillation (Ost)	Saponification NaOH at < 50°C. (Gutsche)
16·0	17·0	14·2
27·0	30·2	27·0
30·8	47·1	43·5
46·9	—	44·5
31·7	48·3	44·6
—	47·3	46·6
45·1	48·4	49·1

These variations impose upon the author the necessity of validating the process finally adopted by the collateral evidences of (1) concordance with the estimation of yield, (2) with the evidences afforded by the test with Fehling's solution (*infra*).

3. *Cupric Reduction* appears to coincide with a degree of acetylation higher than the triacetate (C_6).   The author's observations and conclusions as to the index value of copper reduction in quantitative relation to acetyl are of sufficient importance to be reproduced at length (34-38 of 'Diss.').

Considering the numbers for percentage of acetyl it is clear that they contain results much in excess of those for hexacetate (44·8 p.ct.).   How are these high acetyl numbers to be explained ?

Vignon, Leon, and Gérin have proved that cellulose

nitrates are aldehydic, and therefore reduce Fehling's solution, the present results proving the same for cellulose acetate.

It is well known that by employing various catalysts, aldehydes of the most varying constitution may be acetylated to diacetates. It is also to be noted that in the case of cineol, rupture and acetylation takes place at the ring-oxygen position. In this case of cineol the special catalyst was anhydrous ferric chloride (diss. Transier, Heidelberg, 1907).

On the hypothesis of one or several aldehyde groups we have the explanation of the high acetyl numbers.

In the series of acetylation with (1) 'no catalyst,' and then with (2) copper sulphate, (3) trichloracetic acid, (4) potassium bisulphate, and (5) stannous chloride the maximum numbers are not much in excess of the hexacetate ; only in the case of methylamine sulphate and ammonium persulphate are the much higher results obtained, such as were obtained by Skraup using sulphuric acid ('Berl. Ber.,' 1899, 32, 2413) and by workers in this laboratory, using both sulphuric acid and ferric chloride.

From the tables it will further be noted that these high acetyl numbers are marked by decreased yield, due to solubility in water of acetylated products (of decomposition).

The aldehyde group or groups must be latent as is seen from the fact that cellulose as well as the lower acetyl derivatives are indifferent to Fehling's solution.

The quantitative relations of the copper numbers present important indications. We remark the frequent occurrence of the number 6·3 p.ct. ± 0·5, or a simple multiple of this number. It appears that the liberation of aldehyde groups is not a continuous reaction, but shows interruptions. This is particularly evident for the products obtained with copper sulphate, potassium bisulphate, and methylamine sulphate.

Further, so long as the copper number remains at or about 6·3 p.ct. the viscosities of the solutions are high, but when the copper number reaches 12·6 p.ct. there is a rapid fall of viscosity.

As with viscosity, so also with yield of product.

With copper numbers below 6·3 p.ct. the condition of the acetate, when precipitated by water, is a hydrated jelly (assuming that the acetylation has reached a sufficiently high limit for complete solution in the acetylating mixture). Above the limit, however, of 6·3, for the copper number, the acetate is precipitated in granular form.

Calculating the copper number at 6·3 p.ct. for the acetate, in terms of saponified cellulose acetate, the number is 7·8 p.ct., which agrees with Schwalbe's 7·6 p.ct. for oxy-cellulose ('Berl. Ber.,' 1907, 40, 1347).

Vignon has studied the quantitative reduction of Fehling's solution by nitro-cellulose ('Bull. Soc. Chim.' 1901, 251, 130). He also obtained an interrupted series, and also found that the reduction is independent of the degree of nitration, and is the same for nitro-cellulose as for nitro-oxy-cellulose.

The copper reduction of various sugars have, as is well known, a purely empirical value, and we therefore can attach no definite value to the numbers for cellulose acetate whether 6·3 or 7·8 p.ct. If we assume that 6·3 p.ct. of copper corresponds with each free aldehyde group, and that the cellulose molecule is $C_{24}H_{40}O_{20}$ (see Cross and Bevan, 'Researches on Cellulose,' 1895, 1905) we conclude that with such catalysts as show two interruptions in the copper numbers, viz. 6·2 – 16·6, that in the latter case two aldehyde groups have been resolved.

Beyond this point there is a rapid increase of copper and acetyl numbers, and the viscosity (solution) and yield sink to a minimum.

But there are no further interruptions or sudden increases in the copper numbers. It is curious that in the methylamine sulphate series the last number, 50·7 p.ct., is 6·3 × 8.

Whether the copper numbers above 12·6 are attributable to the cellulose molecule is doubtful. In such cases the products

of the alkaline saponification, the acetates, are partly resinified, or decomposed with formation of acid.

Whether the liberated aldehyde group is acetylated at once, or whether the second aldehyde group is liberated, would appear to depend upon very different factors.

A particular catalyst appears to determine in greater proportion the break-down (potassium bisulphate at 80°), another catalyst favours acetylation (trichloracetic acid at 80°), further, with one and the same catalyst at different temperatures, the liberation of aldehyde groups may be favoured at the expense of the second phenomenon of acetylation.

For the acetate with twelve OH groups $(C)_{24}$ with one aldehyde group acetylated, the theoretical number is 48·7 p.ct. acetyl.

In cases where acetylation and decomposition (Abbau) proceed *pari passu* (methylamine sulphate and ammonium persulphate) the acetylation of the first·aldehdye group (6·3 p.ct.) is complete.

Copper sulphate favours the liberation of aldehyde groups but not the acetylation, whereas in other cases, as in the acetylation of benzaldehyde, the copper sulphate is particularly effective.

In this case the acetyl numbers are in excess of the triacetate, but even when a second aldehyde group is resolved the acetyl number remains constant.

Acetylation carried out at 60° gives lower numbers for acetylation in relation to copper reduction. Possibly, however, the acetylation at 100°C. is so favoured that at this temperature both the first and second aldehyde groups as liberated are simultaneously acetylated.

*   *.   *   *   *   *   *   *   *   *

Upon these investigations we make the following comments :—

As regards the acetylation of the normal cellulose and the 'normal' limit of the acetylation at the triacetate the author justifies his conclusions. The investigation is on a wider experimental basis than those which have preceded it; the conclusions are strengthened by collateral and convergent quantitative evidence. As a matter of fact the general main conclusion was that of our earliest contribution to the subject ('Chem. Soc. J.,' 57, 1, 1890); it was also evident that zinc chloride, the catalyst which we employed, determined a higher limit of acetylation, and the break-down of the cellulose complex was not so rapid as in the case of copper sulphate, methylamine sulphate and ammonium persulphate of the author's series. It is also evident from the present study that the process without catalyst early departs from the normal course.

In view of the results of our later study of the process with zinc chloride as catalyst, which characterise these conditions of acetylation as normal, it would be important to study the later stages of acetylation under the action of this catalyst.

An observation which we have made gives a still greater significance to the particular relation of zinc chloride to cellulose. The higher acetates are hydrated and dissolved by zinc chloride solution with all the features of the attack on cellulose itself. The specific constitution of the complex as a colloid is therefore bound up with the grouping which contains the CO oxygen and the problematical fifth O. atom, and this grouping retains the amphoteric character of the original unaffected by the acetylation of the OH groups.

A conclusion of some bearing on the constitutional problem is warranted by a comparison of the numbers for starch and cellulose. In every respect cellulose is proved to be much the more reactive, not only on the time and temperature factors for a given degree of acetylation, but on the attainment of much higher limits in the extreme cases. Nor does this conclusion fail in view of the sensitiveness of the starch derivatives to the action of the solvents used in washing the crude products, since

the yields are satisfactorily high, though less than in the cellulose series. This conclusion does not accord with a strict interpretation of the general assumption that cellulose represents a ' still larger molecule ' than starch, nor does it accord with the author's conclusion that higher limits of acetylation, beyond the triacetate, are due to the *liberation* and *acetylation* of CO groups of the cellulose complex, or to be more specific : that the reduction of CuO is due to liberated groups of dextrose configuration. If such were the case starch should show a higher limit than cellulose under conditions of action of equal intensity. Moreover, ortho-aldehydic acetates are relatively unstable, whereas we showed that the higher acetates from cellulose are soluble in nitrating acid without change, and are recovered quantitatively ('Chem. Soc. J.,' 1890 : 1). It is quite probable that the problematical fifth O. atom may be involved, and the author himself calls attention to the fact that the cineol ring is attacked by acetic anhydride with $FeCl_3$ as catalyst, and acetylation takes place at the O. position.

In effect this investigation is an empirical quantitative study, with the implied limitation of view of cellulose as a polyhexose aldehyde (anhydride), and does not critically examine the cause or direction of acetylation beyond the triacetate.

INTERACTION OF ALKALI STARCH AND CARBON BISULPHIDE, XANTHOGENIC ESTERS OF STARCH.

C. F. CROSS, E. J. BEVAN and J. F. BRIGGS. ('Chem. Soc. J.,' 1907, 91, 612.)

Reaction analogous to the ' viscose' reaction is determined by the device of first incorporating together dry starch and bisulphide, and then adding the calculated proportion of sodium hydrate in 15-17 p.ct. (NaOH) solution ; the production of alkali starch is sufficiently moderated to allow of intimate in-

corporation of the three reagents before solidification of the mass.

The manipulations for solution of the final product of interaction and the isolation of the starch ester (Na . salt) are identical with those employed in the viscose series. Freed from by-products the compound gives identical numbers in alkalimetric and iodometric titration, the characteristic index of a xanthogenic ester (Cross and Bevan, 'Berl. Ber.,' 34, 1513).

Total sulphur estimated as $BaSO_4$, after oxidation by hypochlorites and referred to the numbers for combined alkali, was in the ratio $S_2 : Na$.

In regard to stability of the xanthate in solution, the characteristic or 'xanthate soda' was estimated (NaOH) at intervals, the solution being kept at the ordinary temperature.

Age of Starch Viscose	Na as XO . CSSNa represented as NaOH p ct. o' original starch
1 day.	19·2
5 days.	10·5
6 ,.	10·3
7 ··	9·0
16 .,	5·2

The following conclusions are drawn :—

The original reaction takes place in the approximate stoichiometrical ratio $C_6H_{10}O_5 : CS_2 : NaOH$. The starch undergoes only slight incidental hydrolysis to soluble derivatives and the proportions precipitated by iodine (as dixanthogenide) closely correspond with those calculated from the original starch reacting. The analogy of the starch with the cellulose reaction is close. The characteristic reaction of starch with iodine enables us to show that no starch is present throughout the stages of decomposition and 'reversion' so long as 'xanthic residues' persist in combination.

On acidifying with acetic acid, and adding excess of iodine,

no colour is developed, but the addition of mineral acid immediately develops the characteristic iodine reaction.

A graphic representation of the stages of reversion would be marked by an asymptotic approach to the line of starch, as of cellulose in the case of viscose. In either case there is a remarkable persistence of fractional residues of the characteristic CSSNa groups, influencing the complex and differentiating its reactions from those of starch.

It might be urged as regards the quantitative relations that these residues are the reciprocal measure of the molecule, or the reacting unit of the carbohydrate, and that this is of indefinitely large magnitude. The alternative view is that the reacting unit is a system homogeneous as regards a particular chemical function, although heterogeneous in actual constitution. This appears to be the simplest way of stating the experimental facts in accordance with the observations that at no stage of the reversion are the products a mixture of starch and its thiocarbonic esters.

ZELLSTOFF VISCOSE UND STÄRKE VISCOSE.

H. Ost, F. Westhoff und L. Gessner ('Annalen der Chem.,' 1911, 382, 340).

Being a condensed account of investigations recorded in greater detail in dissertations of

F. Westhoff : Zur Kenntniss der Viscose und der daraus regenerierten Cellulose.

L. Gessner : Starke Viskose und Alkali-Starke Xanthogenate.

Hannover, 1911.

These investigations, a systematic study of cellulose and starch through their xanthogenic esters, follow of necessity the main lines of our own researches on the viscose reaction and series of resulting cellulose derivatives. In regard to starch the

authors had overlooked our contribution above described, and it will be noted that they independently arrive at the same general results and conclusions.   In addition to the method described by ourselves, they also studied a variety of conditions of interaction from which they conclude that reaction occurs within the wide limits :—

$$1 \text{ mol. } C_6H_{10}O_5 : 2\text{-}3 \text{ mols. NaOH :}$$
$$\text{NaOH} : H_2O = 1/_{19} - 1/_4 \text{ by weight.}$$
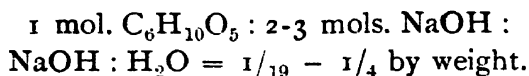
The starch xanthates are isolated by precipitation with alcohol, and in the purified forms are mixtures showing variations in composition as follows :—

calc. to the unit $C_6H_{10}O_5$: $\begin{array}{l} 1\cdot85 - 0\cdot83 \text{ At. S} \\ 1\cdot92 - 0\cdot65 \text{ ,, Na} \end{array}$
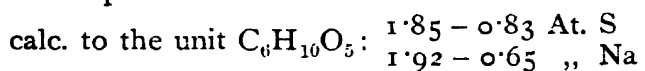
with a general mean $C_6H_{10}O_5 : 1\cdot3 \text{ S} : 1\cdot25 \text{ Na}$

Hence the general conclusions : starch reacts with the alkali to form $[C_6H_8O_3 . (ONa)_2]_n$ and this with CS_2 to the 'normal' xanthogenate

$$\left[C_6H_8O_3 \diagup^{ONa}_{\diagdown OCSSNa} \right]_n$$
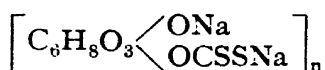
which in solution, and under the treatments for isolation of the 'pure' (homogeneous) product is hydrolysed in the two directions (*a*) with elimination of the ONa residues (*b*) with saponification of the OCSSNa residues and elimination as carbonate, trithiocarbonate, etc. ; these take place at different rates 'a' being higher than 'b'.

The starch is recovered from the purified preparations in approximately quantitative proportions, and dissolved in water at 2 atm. pressure shows rotation $(a)_D = + 196°$. The spontaneous hydrolysis or 'ageing' was observed during a period of twenty days, during which the decomposition moved uniformly. After twelve days the isolated product had the composition $[C_{36}H_{58}O_{28}ONa . OCS_2Na] \frac{n}{6}$. After two months the starch appeared to persist as xanthate in solution.

The solutions on standing show a progressive diminution of viscosity, but without any change in reactions of the carbohydrate such as to indicate conversion into dextrines. The authors express this change, therefore, as a progressive lowering of the value of n in the above polymolecular formulæ.

Cellulose Viscose.—The conditions of reaction are those formulated and studied by ourselves. The results of analyses of the isolated products, and the conditions and results of spontaneous hydrolysis ('ripening'), are closely analogous to those above described for starch. The main conclusions are: the C_6 xanthogenate, assumed by Cross and Bevan to be the original product of interaction, is in effect formed; after one to two days the solution contains the xanthate

$$[C_{18}H_{18}O_8 . ONa . OCS_2Na]\frac{n}{3}$$
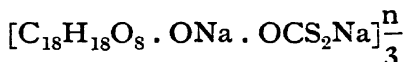
and after five days and immediately preceding coagulation the xanthate $[C_{24}H_{38}O_{18} . ONa . OCS_2Na]\frac{n}{4}$.

In regard to changes of viscosity in the cellulose viscose, the diminution observed in the earlier stages is followed by rapid increase towards the stage of coagulation. The authors, however, consider that the analogy of starch holds, and that a combination of cellulose residues cannot be held to occur; the regenerated cellulose is permanently 'degraded'.

The So-called Cellulose Hydrate. — In the concluding section the authors return to the question of the actual composition of the cellulose regenerated from viscose,—previously treated by them in a special communication ('Ueber die Hydrate Cellulosen,' H. Ost and F. Westhoff, 'Chem. Ztg.,' 1909, 33, 197). Celluloses from various preparations of mercerised cellulose, after prolonged interaction of alkali and cellulose (six weeks to eighteen months), have been analysed after drying at 125°, and the elementary composition found to be uniformly within the limits.

$$\text{C} \quad 44\cdot0 \text{ to } 44\cdot4$$
$$\text{H} \quad 6\cdot32 \text{ to } 6\cdot52$$

Similarly uniform numbers have also been obtained for celluloses regenerated from viscoses, prepared under the widest range of conditions selected to bring into evidence and possible variation of the 'hydration factor'.   The substance shows no variation from the anhydride formula $C_6H_{10}O_5$.

The authors' conclusions are that the term cellulose hydrate has no foundation.   Forms of cellulose show variation of 'humidity constants,' which though not accidental, may be referred to purely physical causes.   The above investigations prove that both with starch and cellulose molecular degradation is determined by the action of alkalis, but without hydrolysis, in the strict sense of fixation of water.

* * * * * * * * * *

Upon these communications we make the following comments :—

The quantitative results recorded may be accepted without reserve.   There are two broad differences of interpretation. The authors maintain for starch and cellulose a ' polymolecular ' formula of unknown but certainly very large dimensions ; the relations of these two compounds, as colloids, to water, and notably their equilibrium with atmospheric moisture, are 'physical' phenomena.   As to the former, it would be out of place on a particular issue to restate our general view that molecular conceptions do not *necessarily* apply to these colloidal forms of matter.   Physical measurements obviously fail to give any results correlative with the reacting unit, and the unit in terms of chemical reactions has continuous functions, that is, dimensions.   In the particular case of the starch xanthate cycle we expressed this fact in the following terms : ' The reacting unit is a system homogeneous as regards a particular chemical function although heterogeneous in actual constitution '.

Not only in this respect, but the depolymerisation of the

complex molecules of starch and cellulose without any change of composition, upon the proof of which the authors lay particular stress, is a view of the observed changes which involves more than one hypothesis of doubtful probability.

In regard to the statement that the term 'hydrate of cellulose' or the view which the term expresses, has no foundation, the alternative is a definition of cellulose as a substance which is an anhydride in constitution, but hygroscopic as an external physical characteristic.

We must again object facts of fundamental significance.

The combination of these colloids with water is a fundamental property; it is attended by thermal effects and modifications of the structural characteristics of the substances, e.g. breaking strain and extensibility; at the same time is independent of minute visible structure. Expulsion of the water thus combined is a dissociation. Mercerisation increases the hydration capacity by a definite proportion, as an ultimate property of the modified cellulose; but the process of mercerisation is a joint reaction of combination with alkali and water, the alkali-cellulose having a very high hydration capacity. The hydrates of cellulose are the most widely distributed of 'natural' substances, and upon this material foundation the activities of the plant world depend in a very important sense. We cannot follow the author in the view that cellulose as a chemical individual only exists at 125°. We prefer to adapt our terminology to the facts of widest significance, because we hold that the significance of these facts must be very much deeper than the science and terminology of to-day which confessedly fails to give any adequate account of these forms of matter.

CELLULOSE AND FORMIC ACID.

The interaction of cellulose and formic acid, as a theoretical problem, suggest many complicating factors arising out of their individual characteristics. These have been rather overlooked in these earlier stages of development of a new group of derivatives which also offer many features of technical interest.

Having investigated ourselves certain of these products, we were impressed with the alternative view, that these points of technical interest were rather overshadowed by the purely scientific interest of the facts disclosed by our investigations, even though only of a superficial and preliminary order.   An account of these preliminary studies is embodied in a communication which being mainly a record of experimental numbers we reproduce *in extenso.*

THE   INTERACTION   OF   FORMIC   ACID   AND CELLULOSE.

C. F. Cross and E. J. Bevan ('Chem. Soc. J.,' 1911, 99, 1450).

Products of interaction of cellulose and formic acid have been described in various communications (Berl and Smith, 'Ber.,' 1907, 40, 906; R. C. Woodbridge, 'J. Amer. Chem. Soc.,' 1909, 31, 1067) and patent specifications, and it is generally assumed that such products are formed by a process of simple esterification.   The probability of formic acid reacting in more than one way should, however, be taken into account, and also, as a factor in the reaction, the labile equilibrium of the cellulose complex and its tendency to change its configuration under the action of reagents (Trans., 1904, 85, 691).

The possible modes of action of formic acid are, in addition to the normal replacement of alcoholic hydroxyl groups by the $O \cdot COH$ residue: (1) As a consequence of the avidity of the acid, an attack on the cellulose complex by hydrolysis or condensation, or by both processes concurrently.   (2) The acid may react through its carbonyl oxygen atom, and give rise to complexes, thus :—

$$\frac{H}{HO}\!\!\diagdown\!\!CO + \frac{H \cdot X}{H \cdot Y} = H_2O + \frac{H}{HO}\!\!\diagdown\!\!C\!\!\diagup\!\!\diagdown\!\!\frac{X}{Y}.$$
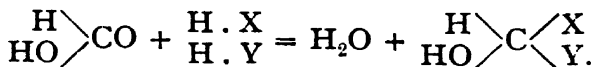
As regards the cellulose we cannot pretend to predict the course of change or the final equilibrium under (1) ; and under (2), if reaction takes place, it suggests the existence in cellulose

or preformation according to (1) of $CH_2 \cdot CO$ groupings. This is an hypothesis justified by well-known transformations of the carbohydrates (as in the production of levulic acid from the hexoses), and more particularly of cellulose under the action of acids.

These considerations have been formulated as the result of an investigation of typical derivatives of this group manufactured by processes already worked on the industrial scale. These compounds are found to be divergent in properties and general characteristics from what might be accepted as the normal, defined from analogy to the better known esters, and especially the acetates.

Experimental.—The products which we have more particularly studied were prepared and supplied to us by Prof. Dr. E. Bronnert (Mulhouse), and were (*a*) a voluminous, white solid, and (*b*) a transparent film, (*a*) being the direct product of interaction of formic acid and cellulose (without catalyst), and (*b*) being obtained by spreading a solution of (*a*) on a glass surface, and evaporating the solvent acid.

Examination of (*a*). The product was soluble in pyridine and nitro-benzene; a characteristic solvent was found in the alkali thiocyanates (for example, of potassium and ammonium); a 20 p.ct. solution of these salts dissolved the compound freely.

When dried in the air the substance contained 8-9 p.ct. of water.

After swelling with pyridine, the action of $N/2$-aqueous-alcoholic sodium hydroxide was rapid :—

Found : Acid (as CH_2O_2) = 44·0. Residue (cellulose) = 76·6.

Cellulose diformate requires acid (as CH_2O_2) = 43·2 ;

Residue (cellulose) = 74·3 per cent.

Under the direct action of the $N/2$-alkali, the saponification is less rapid, and higher acid numbers are obtained (CH_2O_2 = 46 p.ct.) as a result of long-continued action.

On analysis of the anhydrous compound the following numbers were obtained :—

0·1498 gave 0·2425 CO_2 and 0·0712 H_2O.   C = 44·15 ; H = 5·38.

$C_7H_{10}O_6$ (monoformate) requires C = 44·2 ; H = 5·26 p.ct.

These numbers do not correspond with the composition represented by the results of saponification.   In other elementary analyses there was a still closer approximation to the numbers for cellulose, and therefore further divergence from the theoretical numbers for a diformate, which requires C = 44·0 ; H = 4·58 p.ct.   These variations were probably due to the fact that the compound proved to be unstable.

After being kept for four months (in a closed bottle) it was no longer soluble in pyridine, and was found to have developed acidity ; it contained free acid (calculated as CH_2O_2) equal to 10·0 p.ct. of its weight.   After removing this free acid, the compound was boiled with water.   Further volatile acid distilled over, which amounted to 10·8 p.ct., a total of 20·8 ; the loss of formic acid (1 mol.) from a diformate should be 21·1 p.ct.   As an explanation of these results we may assume that the original compound is a monoformate, but of a modified cellulose complex, the second molecule of formic acid, obtained on saponification, being a product of decomposition of this complex, and this is confirmed by the following experiments.

Acetylation.—The compound was mixed with 10 parts of acetic anhydride at 50°, and a 15 p.ct. solution of zinc chloride in glacial acetic acid was added ; the substance dissolved completely.   The solution was boiled in one experiment for one hour, and in a second for five minutes, and the new ester precipitated by pouring into water.

The yield in both cases was the same, namely, 120 p.ct., and corresponds with the subjoined numbers defining the composition of the product.   On analysis :—

0·1725 gave 0·3301 CO_2 and 0·0769 H_2O.   C = 47·48;
H = 4·96.

$C_{11}H_{14}O_8$ (a diaceto-monoformate) requires C = 48·18;
H = 4·75 p.ct.

This diaceto-monoformate neutralised 46 p.ct. of its weight of sodium hydroxide, and gave an insoluble residue (cellulose) = 54·5.   ($C_{11}H_{14}O_8$ requires NaOH = 46; cellulose = 59·1 p.ct.)   The amount of cellulose found was as usual low, owing to unavoidable further hydrolysis.   When dried in the air the compound retained 1·5 to 2·0 p.ct. of moisture, which is within the normal low limits characteristic of the true esters.

The instability of the original ester is thus also shown on acetylation, as one formyl group is displaced when two acetyl groups enter the molecule.

There is, however, further evidence as to the constitution of the original ester, confirming the view that in the reaction by which it is produced the cellulose complex undergoes constitutional modification.

1. A careful examination of the acid products of saponification, using aqueous sodium hydroxide only, showed that acetic acid is produced.   The acid was separated by fully oxidising with permanganate the volatile acids first obtained, redistilling, and finally crystallising the silver salt.   (Found : Ag = 64·85. Calc., Ag = 64·65 p.ct.)

The acetic acid thus formed must be a product of resolution of the new cellulose complex.

2. The cellulose residue showed divergencies from the normal; thus on analysis :

0·1300 gave 0·2133 CO_2 and 0·0810 H_2O.   C = 44·60;
H = 6·93.

The value for hydrogen is an indication of the production of methyl groups, involving, therefore, the migration of hydroxyl groups within the cellulose complex.

This 'cellulose' was acetylated, and gave a high yield (185

p.ct.) with an exceptionally high acid number on saponification [acid (as $C_2H_4O_2$) = 81·1] and correspondingly low cellulose residue (27·3). These numbers and relations are sufficient to indicate the more complex nature of the interaction of cellulose and formic acid (*supra*). Further investigation is required for the full elucidation of the constitutional modification which cellulose appears to undergo.

Examination of (*b*).—This was a transparent uniform film of 0·085 mm. thickness. From the dimensions we were able to estimate closely the volume of a given weight, the specific gravity being found to be 1·520; that is, in the normal air-dry state. The moisture retained in this condition was 13·0-16·0 p.ct. Both figures are widely divergent from those generally characteristic of the cellulose esters. The film was found to resist the general solvents of these esters, as well as the special solvents noted for the product (*a*). Analysis gave:—

Anhydrous substance:—

0·1281 gave 0·2052 CO_2 and 0·0744 H_2O. C = 43·7; H = 6·4.
0·1454 „ 0·2355 CO_2 „ 0·0812 H_2O. C = 44·1; H = 6·2.
$C_6H_{10}O_5$ requires C = 44·4; H = 6·1 p.ct.

Air-dried substance:—

0·1579 gave 0·2224 CO_2 and 0·0988 H_2O. C = 38·4; H = 6·8.
$C_6H_{10}O_5$ + H_2O (15·8 p.ct.) requires C = 38·39;
H = 6·85 p.ct.

So far, therefore, there is nothing to identify this product as an ester; it has the composition and properties of a cellulose.

Saponification of the substance with $N/2$-aqueous-alcoholic sodium hydroxide proceeded with some difficulty. The following results were obtained:—

Duration of boiling	Acid formed, calc. as CH_2O_2
9 hours	25·0
Further 6 „	12·1
„ 4 „	4·4
	41·5

These results indicate a course of action different from the saponification of an ester : rather a progressive decomposition of a cellulose complex with production of acid groups.

With the view of elucidating this point, we carried out some experiments on the interaction of formic acid and typical celluloses.

(*a*) Cotton, wood, and esparto celluloses were taken as types of the generally accepted classification. The action in these cases is slow, and accompanied by considerable discoloration (brown). Products of condensation are formed. The fibres gelatinise, showing progressive hydration, and the action differs markedly from that of other acids comparable in general functions with formic acid.

On treating with water and washing, we obtained :—

Percentage of original			Cotton	Wood Cellulose	Esparto
Insoluble product	.	.	99·0	91·0	82·5
In solution	.	.	5·7	11·4	—
Total	·	·	104·7	102·4	
Saponification of insoluble product :					
yield of acid as CH_2O_2	.	.	18·11	22·45	26·2

It is to be noticed that with a small gain of weight due to the fixation of the formyl residue, there is a relatively large production of acid on saponification. In other words, the celluloses are constitutionally modified, and, as a result, are decomposed by alkalis with the formation of acid products.

(*b*) Cellulose (hydrate) regenerated from solution as xanthate (viscose).

On digestion at 60° there is a very gradual attack, the cellulose passing into a viscous solution. On dilution, the product is precipitated. The following determinations were made :—

1. Twelve hours' digestion—incomplete solution.

2. Twenty-four hours' digestion—nearly complete solution.

	(1)	(2)
Reprecipitated	89·4	85·42
Products in solution:		
(Residue on evaporation) . .	20·4	35·80
	100·8	121·22

The insoluble product from (2) on saponification showed acidity equal to 44·00 (calc. as CH_2O_2). These numbers and incidental observations lead to the conclusion that this form of cellulose (hydrate) is attacked without formation of condensed coloured products. There is no discoloration, even on raising the temperatures to 100°, and the viscosity persists when the heating is long continued; at the same time a portion of the cellulose is degraded to soluble products of low molecular weight. These products were acid in higher proportion. We have also made a *comparative* study of the interaction of formic acid (99 p.ct.) and the hydrated celluloses obtained from solutions in cuprammonium, and as xanthic ester (viscose). These show similar behaviour. With the acid alone, prolonged digestion at temperatures up to 45˙ failed to effect more than partial solution (30 p.ct.). The presence of catalysts effects a marked change. With 20 parts of the acid containing 2 p.ct. of zinc chloride in solution, a homogeneous product was obtained in twenty hours' digestion at 45°. The purified product was analysed :—

0·1713 gave 0·2758 CO_2 and 0·0716 H_2O. C = 43·91 ; H = 4·65.

A diformate requires C = 44·0 ; H = 4·58 p.ct.

With phosphoric acid the action is especially rapid. In a typical case, we obtained a yield of 116 p.ct. of the insoluble product, which on saponification gave, acid (as CH_2O_2) = 49·5 and residue (cellulose) = 56·4 p.ct.

Owing to the difficulties inherent in investigations of cellulose products it will be necessary to extend these observations to other polyhydroxy compounds of which the products of

possible decomposition are better known, or which, from simplicity of molecular structure, can be studied in relation to synthetic reaction with greater precision of data.

In one direction we have examined starch, which shows many analogies to cellulose in its reaction with formic acid; products insoluble in water are obtained, and these also, on saponification, show acidity in excess of the molecular proportions of acid actually combining. We have also studied certain aromatic compounds under similar conditions of interaction, and although there is no direct relationship of these to cellulose, it is well known that, through the ligno-celluloses, there are many suggestions of a cyclic constitution of cellulose.

The following is a brief account of the results obtained with typical aromatic hydroxy compounds.

Resorcinol reacts with formic acid, and in the presence of hydrochloric acid the change is rapid, a substance being formed with considerable development of colour (crimson). The main product is easily isolated by crystallisation from water :—

$$0.1482 \quad \text{gave} \quad 0.3397 \quad CO_2 \quad \text{and} \quad 0.0714 \quad H_2O. \quad C = 62.5;$$
$$H = 5.3.$$
$$C_{13}H_{12}O_5 \text{ requires } C = 62.9; \quad H = 4.8 \text{ p.ct.}$$

The formula suggests that the compound is a *dihydroxybenzhydrol*, formed according to the equation :—

$$2C_6H_6O_2 + CH_2O_2 = HO . CH[C_6H_3(OH)_2]_2 + H_2O.$$
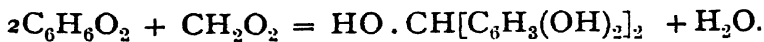
The alkaline solutions of this substance are very strongly coloured (crimson). The *penta-acetyl* derivative was recrystallised from alcohol :—

$$0.250 \text{ gave } C_2H_4O_2 = 67.2.$$
$$C_{23}H_{22}O_{10} \text{ requires } C_2H_4O_2 = 65.5 \text{ p.ct.}$$

Quinol gives no reaction under similar conditions, and it appears, therefore, that condensation takes place in the para-position with respect to a hydroxyl group. This is confirmed by experiments on α- and β-naphthol. The latter does not

react with formic acid, whilst the former gives a small amount of a condensation product, which is insoluble in water, but reacts with alkalis, giving grass-green solutions.   The reaction of the naphthols with acetaldehyde are analogously divergent (Claisen, Ber., 1886, 19, 3316).

Phloroglucinol reacts rapidly, but the first product appears to be phloroglucide (Found, C = 61·3 ; H = 4·0.   Calc., C = 61·4 ; H = 4·2 p.ct.), which would be formed according to the equation :—

$$2C_6H_6O_3 = C_{12}H_{10}O_5 + H_2O.$$
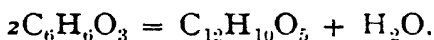
With resorcinol and phloroglucinol in molecular proportions, we obtained intermediate results ; the main product after crystallisation was analysed :—

0·1360 gave 0·3229 CO_2 and 0·0468 H_2O.   C = 64·7 : H = 3·8.
$C_{13}H_{10}O_5$ requires C = 63·4 : H = 4·0 p.ct.

This compound is probably formed according to the equation :—

$$C_6H_6O_2 + C_6H_6O_3 + CH_2O_2 = C_{13}H_{10}O_5 + 2H_2O.$$
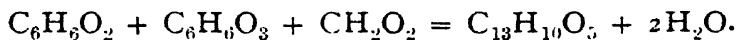
To connect these observations with cellulose it is only necessary to remember that the CH . . . OH(1 : 4) grouping of a phenol alternates with, and, in fact, reacts as, the grouping CH_2 . . . CO, and a ketene grouping has been shown by ourselves to be definitely characteristic of the ligno-celluloses and inferentially of the celluloses ('Cellulose,' 1895, and 'Researches on Cellulose,' I. and II., 1900-1905).   Collie has developed the potentialities of the ketene and multiple ketene group from a broader point of view, and applies his conclusion to the carbohydrates, including cellulose (Trans., 1907, 91, 1806).

From the results so far obtained we may conclude that the formyl derivatives of cellulose are not the analogues of the acetates, the reactions of formation certainly introducing other factors which we have indicated, and our further investigations

will have reference to the influence of these, as a working hypothesis.

Incidentally, these results suggest a clue to anomalies, and the apparently contradictory results of investigators in regard to the acetates of cellulose (Berl and Smith, loc. cit. ; Ost, 'Zeitsch. angew. Chem.,' 1906, 19, 993 ; J. Gutsche, 'Diss.,' Göttingen, 1910), which we shall discuss in a subsequent communication.

We are indebted to Professor Bronnert for the supply of products as stated, and we have pleasure in acknowledging experimental results included in this paper from Mr. S. S. Napper, and our indebtedness to Messrs. S. Courtauld & Co. for their valuable collaboration. We wish also to mention the efficient services of our assistant, Mr. D. R. Davey, throughout these investigations.

*   *   *   *   *   *   *   *   *   *

In this research we have chiefly endeavoured to accumulate verified numbers, and to avoid any prejudgment of the facts based upon rigidly systematic views of ' cellulose ' as containing no potentialities beyond those of a multiple dextrose (or anhydro complex of the hexose units).

The question in fact always presented to the investigator by cellulose is, What is the kind and degree of constitutional modification determined by reaction ?

The extreme view is that cellulose is appreciably modified by every reagent with which it comes in contact ; that it is labile or plastic in such degree as to respond to the feeblest of attacks by some change of configuration. If this is an extreme view, it is much more ' practically ' suggestive than the opposite extreme, according to which it is chemically inert, and only brought into reaction under conditions of a certain intensity. We have dealt with some aspects of this problem in our discussion of ' the normal cellulose,' and we shall revert to the 'practical ' issues involved in the concluding chapter.

As regards formic acid the experimental facts suggest that it determines interior changes in the complex comparable with

those of dextrose under alcoholic fermentation, a migration of H and OH tending to produce methyl groups in the one direction and carboxylic groups in the other. Such a change would increase the amphoteric activity of the complex, and this is so far confirmed by the solubility of the derivatives in 'neutral' saline solutions such as the thiocyanates.

In this aspect of the activity of formic acid, there is some analogy with the action of hydrobromic acid and the production of methylated furfural derivatives (Fenton), but without the complication of condensation and ultimate resolution of the complex to unit groups, due to the specific avidity of the halogen hydracid for H_2O.

On the contrary, the evidence of associated physical changes points to the conclusion that this tendency of the acid, also of relatively great avidity, is counteracted by 'hydration'. The derivatives which we have examined are characterised by high proportionate constants of humidity, higher even than those of the original celluloses, and exceptionally divergent from the general rule obtaining in the region of esters. We would here remark in further emphasis of the conclusions on p. 35 that these 'humidity' constants are an index of constitution; they represent combined water and not a 'physical' phenomenon; the compounds are 'hydrates'. This may be noted in correlation with the specific hydration capacity of formic acid to the limiting orthoacid $H . C(OH)_3$.

On the problem of possible synthesis by interaction of the acid as $H . OH . CO$ with groups of the original complex, or modified under reaction in the directions indicated, we can only note its suggestiveness first in explaining some of the experimental facts recorded, but further in relation to the fundamental facts of plant physiology. Formic acid being the obviously first stage in the deoxidation of carbonic acid, the probability of its playing a specific part in the carbon assimilation of the plant cell cannot be overlooked. The view that formaldehyde is the actual first product of deoxidation is of course more attractive, and has been more and more generally adopted since its direct condensation to hexoses has been studied.

('Ueber dei Rolle des Formaldehyds bei der Assimilation der Pflanzen,' O. Loew, 'Berl. Ber.,' 1889, 22, 482.)

It is perhaps more attractive for the psychological reason that it appears to provide a chemical mechanism of carbohydrate synthesis, and a mechanism independent, *qua* synthesis, of the plant protoplasm. It must, however, be borne in mind that the synthesis of carbohydrates and cellulose, though a major effect, is not the all-inclusive problem of assimilation. To mention only one of its correlative problems, the production of fats and oils and the equivalence of their functions with those of the carbohydrates in relation to the living organism, animal as well as vegetable, are outside our present range of knowledge.

A contribution to carbon synthesis from this second possible active cause is a useful working hypothesis and a suggestive basis for revising and extending some of the views of plant physiologists which in the absence of positive chemical evidence rather tend to a narrow and sterile exclusiveness.

CHAPTER IV

Further investigations of quantitative reactions of the fibrous ligno-celluloses have been carried out by the authors, more particularly of the reactions with the halogens, with phloroglucol and with acid hydrolytic agents. The numerical results are 'constants' of the lignone complex for which a general schematic view may be formulated.

The constitutional formulæ proposed by Czapek and Klason are critically discussed.

The autoxidation of the ligno-celluloses has been investigated by the late W. J. Russell, and the results of his investigations are noted, more particularly with reference to a general study of these phenomena upon which they are a reaction of the ethenoid groups of the lignone complex.

Other contributions of sectional import are noticed, including a study by the authors of a well-known effect of damage to commercial jute, which, however, as a document primarily of industrial import is printed in the next chapter.

LIGNO-CELLULOSES AND THE HALOGENS.

FROM the results of earlier investigations of the interactions of the typical ligno-cellulose and the halogens, as described in 'Cellulose' (1895), the following points of general importance appear as established : The reactions take place only in presence of water. In the case of chlorine the function of the water is limited to hydration or hydrolytic effects. There is no evident indirect oxidation of the fibre substance as a result of inter-action of Cl_2 and H_2O. The reaction is quantitatively simple ; the lignone complex is attacked selectively and the chlorinated derivative is homogeneous ; the cellulose is unattacked and is isolated with maximum yields, and in the cellulose complex the

less resistant β cellulose is conserved. With bromine (also in presence of water) the specific reaction of combination is much less intense, whereas the secondary reactions of oxidation are evidenced by much increased production of hydracid, and lower yields of cellulose. In applying the reagent to the isolation and estimation of celluloses, from compound celluloses, Hugo Müller had shown ('Pflanzenfaser,' 1873) that the halogen is sensibly without action—i.e. the indirect action of oxidation—upon cellulose, but only under carefully limited conditions of action.

Iodine reacts rather by way of absorption, the combination with the lignone being of the feeble order of 'adsorption' compounds. Nevertheless, under uniform conditions it is constant, and our own investigations in the case of the typical ligno-cellulose reduced the constant to an empirical definition as follows :—

Digested at 18°C. with twenty times its weight of $\frac{N}{10}$ iodine, in solution in aqueous potassium iodide, the absorption is constant at 12·9-13·3 p.ct.

It may be noted that the corresponding equivalents for the more reactive halogens would be approximately, bromine 8·0 p.ct. and chlorine 3.5 p.ct.

In view of the importance of these reactions and their relation to the question of a 'normal cellulose' and methods of isolation—questions fully discussed on pp. 27-38—we have made observations on the reactions with bromine.

The ligno-cellulose was boiled with 1 p.ct. aqueous NaOH, washed thoroughly and digested in the cold with excess of an $\frac{N}{10}$ or 0·8 p.ct. aqueous bromine, for sixteen hours.

After estimating the excess of bromine, the free bromine was expelled. The HBr was estimated in the solution, and the combined bromine in the brominated ligno-cellulose.

Bromine combined and adsorbed p.ct. of actual ligno-cellulose   32·0
Bromine in combination with ligno-cellulose   .   7·7
Bromine as hydrobromic acid   .   .   .   .   22·5
                                                        ─────
        Total accounted for   .   .   .   30·2

The proportion *combining* is approximately equivalent to the iodine *adsorbed* under parallel conditions ; but in addition to the reaction of combination there are two equivalents to account for as hydracid, which therefore may be taken to measure oxidation.

On the other hand, a large number of quantitative determinations of the chlorination factors have established equivalent relations for the halogen combining and the halogen converted into hydracid, viz. approximately 8 p.ct. on the same basis of calculation.

This is approximately the double equivalent of the bromine as halogen combining, and the equivalence of the hydracid excludes the possible factor of indirect oxidation, under the more intense and specific action of the chlorine.   As a more satisfactory comparison of intensity of action of the two halogens we isolated and analysed the brominated derivative, and found it to contain Br. 23·3 p.ct. (compare Cross and Bevan, 'Chem. Soc. J.,' 1882, 42, p. 96). Our numerous analyses of the lignone chloride have given uniformly Cl 26·7 p.ct.   These numbers are in accordance with our view that the group combining presents two points of attack to the halogen, an ethylene position—CH = CH—and a CH_2 in para-position to a CO the product being a quinone chloride.

In reference to the isolation of cellulose.   Under the conditions prescribed by H. Müller (loc. cit.), the digestions with bromine water (followed by boiling with aqueous ammonia) require to be several times repeated (two to five times) for the final elimination of lignone.   The action of the bromine may be intensified by applying it in more concentrated forms ; thus in a Br atmosphere or in contact with Br-Aq at 1-2 p.ct. Br,

the absorption of the halogen reaches the higher limits of 30-50 p.ct., and after washing and treatment with alkaline sulphite of soda a 'pure cellulose' is obtained. But the yields are 2-3 p.ct. below those from chlorination, and that this is due to oxidation is shown by the high ratio of HBr formed to Br combining. Lastly, we have in our investigations of 1878-1882 (loc. cit.) called attention to the influence of the factors of oxidation and hydrolysis, as generally associated with processes of cellulose isolation. In the chlorination process oxidation is very much limited if not entirely absent; but we showed that by lowering the temperature of reaction to 0°, and by treating with sulphurous acid immediately after chlorination, the yields of cellulose from normal jute may be increased up to 82-83 p.ct. These treatments minimise the hydrolytic action of the hydracid produced, and possibly also incidental slight oxidations. The effect is to conserve residues which otherwise would be degraded from the condition of 'cellulose' to alkali-soluble modifications.

LIGNO-CELLULOSE AND CHROMIC ACID—ACETIC RESIDUE.

In our first volume 'Cellulose' (1895) we have described the carefully restrained actions of chromic acid upon the typical ligno-cellulose. The conditions of action were dilute aqueous solution at ordinary temperatures; (*a*) the CrO_3 alone, (*b*) in presence of added acetic acid, (*c*) in presence of H_2SO_4 at $N/1$ concentration.

Under oxidation of this feeble intensity the lignone complex is entirely broken down to products of low molecular weight, chiefly acetic and oxalic acids, with considerable evolution of gaseous products when the proportion of CrO_3 present is large. The oxidation under these conditions extends to the cellulose which is profoundly attacked.

Those reactions appear to us to be more important than is

generally recognised, in their bearings on the constitution of the lignone complex. The aromatic or benzene hydrocarbon rings are resistant to oxidation by chromic acid, under conditions of considerable intensity. The groupings suggested by Klason and Czapek would produce aromatic oxidation products, acids of unmistakable identity.

The complete destruction of the characteristic constituent groups of the lignone complex under such oxidations as we are considering, relegates them to another constitutional class.

In some recent researches towards a closer definition of the constitutional relationships of the 'acetic residues' of the lignone complex ('Cellulose,' 1905, p. 191), we have made quantitative determinations of the simpler products of those oxidations under the conditions of interaction as under :—

Jute fibre 100 ; CrO_3 42 ; water 1900 ; H_2SO_4 100—total volume 2000 c.c. at 16°C. ; digested forty-eight hours. The yield of fibrous residue ('oxycellulose') was 79 p.ct. ; the net loss of the ligno-cellulose therefore 21 p.ct.

Acetic Acid.—The total volatile acid, originally distilled from the solution and calculated as acetic acid, was 6·0 p.ct. of the ligno-cellulose.

A second fraction of the solution was treated with CrO_3 in excess, digested for some hours at 90-100° and then distilled. The volatile acid was reduced to 5·2 p.ct., by oxidation and removal of formic acid.

Oxalic Acid was isolated as BaC_2O_4 : the precipitate decomposed by acid, and the oxalic acid precipitated as CaC_2O_4 in presence of acetic acid.

Oxalic acid $H_2C_2O_4$, 4·8 p.ct. of the ligno-cellulose.

Carbonic Acid was estimated in independent experiments under identical conditions : (*a*) By measurement of gas evolved ; (*b*) by loss of weight of apparatus, the CO_2 escaping through tubes containing H_2SO_4 ; (*c*) by absorption in $Ba(OH)_2$ and weighing the $BaCO_3$ precipitated. The results were (*a*) 3·0 p.ct.,

(*b*) 4·1 p.ct., (*c*) 4·0 p.ct.   To these products we have to add the H_2O produced by the combustion, and CO which was not estimated.

If we take into consideration the approximate molecular proportions of lignone ($C_{19}H_{22}O_9$) and CrO_3, viz. 100 ligno-cellulose = 20 lignone, and the latter oxidised in the ratio $C_{19}H_{22}O_9 + 2CrO_3 = O_3$, the major proportion is accounted for in terms of these simplest products.   Traces only of aromatic products are present.

Another consequence of this statistical method is to show that as relatively little oxygen is consumed in what appears to be a very destructive oxidation, the part played by water (hydrolysis) must be considerable, and we have given expression to this in the prevalence of $CO . CH_2$ groupings in the constitutional formulæ we have proposed.

Our chief object in this investigation was to fix the maximum proportion of 'acetic residues' in the lignone complex.   Acetic acid is a product of the attack of all hydrolytic reagents, even the simplest.   In the confirmatory researches of Cross and Tollens (*infra*, p. 121) this is taken as evidence that the groups yielding the acid are definitely present as $CH_3 . CO . O$.   But we have always hesitated to draw this conclusion.   After alkaline treatment there is no evidence of a proportionate increase of OH groups in the lignone : and in the chlorinated derivative the proportion of OH is easily ascertained to be a minimum.   Keeping to the more general ketene formula $CO . CH_2$ for these residues we revert to the question of quantitative proportion.   We consider that the 5-6 p.ct. obtained as *Acetic Acid* under chromic oxidation is the probable maximum.   We note that this fairly accords with the maximum yield under destructive distillation.

We note also that the proportion to lignone is high—not less than 30 p.ct. : and this is so obviously the expression of an essential constitutional factor, that it is difficult to account for

the statements of Klason, *infra* It is clear also that we cannot accept any constitutional formula for the lignone complex which does not take this into account.

The perennial woods or woods proper are equally and proportionately characterised by the acetic residue: it is true that the lignone of coniferous woods is differentiated somewhat from the type represented by beech wood: the acetic residue is in somewhat lower proportion and the chlorinated derivatives differ also in reactions, and the oxidation factor under chlorination is higher.   But these are minor divergences.

Summing up the present and previous discussion of this complex problem, we submit a general or schematic constitutional formula for the lignone of the typical ligno-cellulose :—
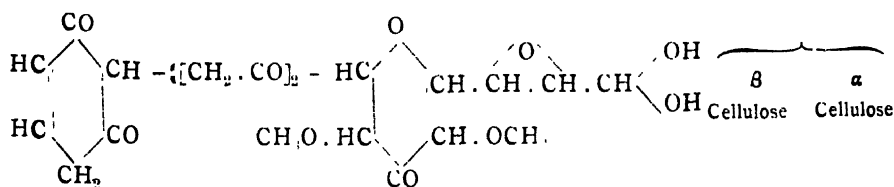
This takes into account the quantitative reactions of chlorination, resolution by bisulphites, production of acetic acid (hydrolysis and oxidation), estimation of methoxyl (hydrolytic acid) and hydroxyl (esterification).

It may be noted by way of further explanation : in the bisulphite reaction the cleavage is on a different line from that under chlorine : the β cellulose is taken into the soluble complex : by chlorination it is conserved in union with the α cellulose.

The β cellulose is a furfuroid, and contains also $O . CH_3$ groups.   This would explain the higher proportion of $O . CH_3$ groups determined in the sulphonated lignone derivatives, the soluble by-products of the bisulphite (cellulose) process.

BEITRAGE ZUR KENNTNISS DER CHEMISCHEN ZUSAMMENSETZUNG DES FICHTENHOLZES.
P. KLASON (Berlin, 1911).

This is a special study of the chemistry of the wood substance (pine wood), the results being integrated in terms of a constitutional formula. A résumé of results of the author's researches is preceded by a general historical survey and summary of researches in chronological sequence in which the contributions of Schweizer, Frémy, Payen, Schultze, Erdmann, Wiesner, M. Singer are noticed, as well as the inventors of processes of technical importance, e.g. Tilghman, Ekman, Mitscherlich.

The investigation of the by-products of the bisulphite process (cellulose) has led the author to assign to ' lignin' the statistical formula $C_{40}H_{42}O_{11}$.

From a consideration of its reactions and their analogy with those of coniferyl alcohol, the constitution of lignin may be derived from the latter which is :—

$$C_{10}H_{12}O_3 = \begin{array}{c} CH:CH.CH_2OH \\ OCH_3 \\ OH \end{array}$$

[Tiemann]
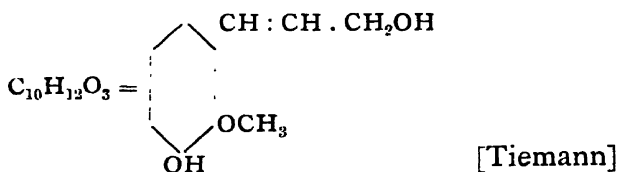
Four such units are assumed to be condensed with elimination of $3H_2O$, and $2CH$ groups oxidised to $2COH$: i.e. $4C_{10}H_{12}O_3 - 3H_2O + O_2$.

The author's summary of results of his investigation we translate *in extenso* :—

Pine wood yields to boiling water 12 p.ct. of its weight (dry) of constituents made up of wood gum (10 p.ct.) and bodies closely allied to lignin (2 p.ct.) : the 'wood gum' of coniferous wood is only slightly soluble in aqueous alkalis, in contradistinction to the woods of foliage trees : it contains as constituent,

aldose groups, xylose (with arabinose) (25 p.ct.), mannose (16 p.ct.), galactose (traces) but chiefly dextrose.   The water-soluble lignin components are made up of coniferyl alcohol and of a condensed anhydride of oxy-coniferyl alcohol or allied compound.   The 'lignin' of the wood is not, as is gener-ally assumed, in combination with carbohydrates.   Lignin is not homogeneous but contains at least two main constitu-ents, which probably however only differ in the substitution of $O . CH_3$ for OH.   These are of high molecular weight and from observations on sulphonated derivatives, not less than 4000 :   in regard to these derivatives the formula weight $C_{40}H_{43}O_{11}$ combines intimately with $2SO_2$, less intimately with a 3rd SO_2 group and feebly with a 4th.   From observations of iodine absorption the compound appears to have 3 ethylene groupings.   The lignin sulphonates present in the by-products of the bisulphite process have the composition $C_{40}H_{44}O_{17}S_2Ca$ whence the formula for lignin $C_{40}N_{42}O_{11}$.

The above-described investigations were first published in Sweden in 1907 ('Arkiv. f. Kemi.,' Bd. 2, 1907).

In an appendix the author discusses subsequent publications on the same subject.

Czapek obtains a product in fractional quantity by treating finely divided wood with solution of stannous chloride.   This product showing the characteristic reactions of lignin he terms hadromal ('Ztschr. Phys. Chem.,' 1899, 27, 141) and indicates its close constitutional relationships to the vanillin group.   Further investigated by V. Grafe ('Sitz. ber. Wien.,' 1904, I. 113, p. 253) hadromal is a mixture of vanillin, pyrocatechol and methyl fur-fural.

These results are found to be so far reconcilable with the conclusions above set forth, methyl furfural being a product of decomposition of carbohydrates and vanillin of coniferyl alcohol, that is of actual constituent groups of the wood substance. But the author cannot accept the view that the wood complex

is made up of these aromatic groups together with methyl furfural in 'glucoside' combination with cellulose. The colloidal character of the wood substance has to be taken into account : and the evidence goes to show that lignin is not in chemical union with cellulose. Attention is then directed to the recent contribution of H. Wislicenus ('Ztschr. Chem. Kolloide,' 1910, 6, 1) towards the elucidation of the actual processes of formation of ligno-cellulose in the plant. Accepting the general view of these processes as an adsorption synthesis there is neither logical necessity nor objective basis for the further conclusion that this deposition of colloidal constituents of the procambium implies a cellulose in 'adsorption' union with a chaotic mixture of products. Lignin appears from the results above outlined to be relatively simple, as is cellulose in its ultimate composition, and the author maintaining as further evidence of their correctness that they furnish fundamental data for control of the bisulphite process of cellulose manufacture.

In conclusion he re-examines his views of the constitution of lignin in relation to its condensation with phloroglucol (Cross, Bevan and Briggs, p. 116). Taking pine-wood as containing 50 p.ct. cellulose and '28 p.ct. of lignin of high molecular weight' he calculates a theoretical combining ratio. Lignin : phloroglucol = 100 : 23·2 as against 27·5 p.ct. actually resulting from the experimental numbers of Cross, Bevan and Briggs, which is a sufficiently close concordance.

* * * * * * * * * *

Our comments on this communication are as follows :—

Full weight should be attached to the author's quantitative results ; but his conclusions as to the constitution of the lignone complex have only the interest of a speculative discussion. That they cannot be accepted as even an approximation to the solution of the main problem is evident from the absence of the evidence in verification which should present no difficulty. A purely aromatic complex such as that assumed would readily

yield protocatechuic acid and phenols on fusion with alkalis, and well-characterised derivatives on products of oxidation, bromination and even hydrolysis.

The full study of the chlorination of the typical ligno-cellulose, which is in all respects a quantitative resolution, proves that chlorination is limited to one group in a complex of C_{19} dimensions from which traces only of benzene derivatives can be obtained.   These systematic studies have been entirely overlooked by the author.

But he also fails to diagnose the acetic residues as an essential constituent of the complex.   He states positively that the lignone complex (of coniferous woods) yields no acetic acid on oxidation.

Although this particular lignone is characterised by a lower proportion of these residues, this is a divergence in degree only but *pari passu* with other features of divergence from the prototypes of the ligno-celluloses which are the jute fibre substance, in 'annual' products, and beechwood in products of perennial growth.

That the sulphonation does not take place in the oxidised hydro-aromatic groups, accords with the observation that these lignone sulphonates are brominated in similar molecular proportion to the original.   In reference by comparison to our schematic formula (p. 104), a pyrone or hydropyrone group is in accordance with the results of destructive distillation and the ready formation of acetone at comparatively low temperatures.

Of other characteristic reactions it is to be noted that the typical ligno-cellulose (Jute) is not readily attacked by alkaline cupric oxide (Fehling's solution) and this is interpreted in the above scheme by the absence of free aldehydic groups.   It must also be emphasised that we do not propound a molecular constitutional formula, and assign no dimensions to the typical groupings of the above scheme.   Each group is probably complex, and the aromatic component for instance may very well be of $3C_6$ dimensions united by CO oxygen linking, the mode of union of the typical groups of the lignone scheme to

one another, as to the cellulose groups, to constitute our ligno-cellulose aggregate, is obviously indeterminate.

It is indeed an open question whether the lignone is in definite union with the cellulose residues, e.g. as acetal, lactone, ether or ester, complexes, or whether the bond of union is not rather of the type of solid solution, which in the case of colloidal compounds may very well represent a state of combination quite distinct from that of mixtures however intimate. Such a view in fact would rather conform with the views of Wislicenus ('Ztsch. Kolloide,' 1910, see p. 110) that the ligno-celluloses are by their origin and chemical 'habit' adsorption compounds. In formulating this view, however, we do not find that Wislicenus has drawn upon the strongest evidence which is afforded by the full statistics of any one of the quantitative reactions of the ligno-cellulose.

Thus in chlorination there is only slight ascertainable hydrolysis or hydroxylation of the complex or its components. The increase of weight determined is approximately that calculated for the chlorine combining. The lignone chloride $C_{19}H_{18}Cl_4O_9$ acetylated under most favourable conditions, combines with 1 mol. acetyl, and the acetylation is not necessarily due to an alcoholic or phenolic OH group (CHOH) but may take place at one of the CO or H.CO positions. The latter is the more probable from the fact that no benzoate is obtained by treating with benzoyl chloride in presence of alkalis.

In the typical ester reactions—more especially nitration and acetylation—the ligno-cellulose behaves as a mixture of cellulose—$C_6H_7O_2 . OH_3$—which reacts, and the lignone complex which is only fractionally affected.

Thus the nitration of purified jute fibre shows an increase of weight of 45 p.ct. and the product contains 12 p.ct. of nitric N. Assuming that the reaction is confined to the cellulose (80 p.ct.) this represents an increase of 82 p.ct. and a percentage of N = 13·9 which numbers are closely approximate to those for the maximum nitration of cellulose.

The acetylation and benzoylation of the ligno-cellulose complex yield esters in which combination is definitely localised

in the cellulose groups, and with only slight incidental modifications of the lignone complex. These reactions have been fully discussed in a previous volume ('Researches,' I., 1901, pp. 125-135), and we do not reproduce the results in further detail.

The feature of these observed relationships to be insisted upon more particularly, is the extraordinary intimacy of the union of cellulose and lignone, notwithstanding the absence of any ascertainable combination of their constituent reactive groups. Not only does this hold for the original complex, but even when modified by esterification of the cellulose OH groups in the diversified range of reactions above discussed. This is especially marked in the reaction of nitration which might be expected so to differentiate the constituent groups as to allow of simple fractional resolution by solvents. So far from this being the case, the complex is found to behave as a homogeneous mixture even when fractionated by alkaline reagents ('Researches,' I., p. 134).

LIGNO-CELLULOSE—AN ADSORPTION COMPOUND.

H. WISLICENUS and M. KLEINSTÜCK ('Z. Ch. Ind. Kolloide,' 1910, 6, 17-23, 87-94. Abs. 'J. S. C. I.,' 1910, 268).

The authors find that when wood sap is shaken with cellulose or with fibrous alumina, constituents of the sap are adsorbed. These phenomena were studied in great detail in the case of sap from various sources and at various seasons and it is concluded that wood substance is formed by adsorption of colloidal substances from the cambial sap by the cellulose which is first formed, and also by the deposition of membranes on its surface formed from colloidal products of assimilation. They consider that purely chemical phenomena play a subordinate part in the process. Lignin is regarded as a varying mixture of colloids adsorbed by the cellulosic framework in a partly reversible, partly unreversible state. The spring sap appears to be a partial reversal of this deposition process and

contains comparatively small amounts of dissolved colloids before the period of foliage development. On the other hand, during the period of wood formation, the cambial sap contains large amounts of adsorbable colloids which decrease in quantity in August when wood formation ceases.

LIGNO-CELLULOSES AND PHOTO-CHEMICAL PHENO-MENA.

We cannot close this theoretical account of the ligno-celluloses without introducing the researches of the late W. J. Russell on 'The Action of Wood on Photographic Plates in the Dark' (' Phil. Trans. B.,' 197, 281, 1904; also · Proc. R. S. B.,' 78, 385; 80, 376).

We are indebted to Mr. W. F. Bloch, who assisted Dr. Russell in these investigations, for the following notes of their results :—

Russell found that all the woods were able to give definite pictures upon a photographic plate, in absence of light.

The action takes place when the wood is kept at a considerable distance from the plate; but for perfect definition, contact was necessary. The pictures usually corresponded with the visible structure of the wood ; but in some cases there was a marked differentiation.

This selective activity appeared to depend in part upon the resinous constituents of the wood and its disposition in the cells ; but also in part upon the nature of the cell-wall structure itself, which in cases offered much resistance to the passage of the active bodies.

On the evidence, the active bodies must be regarded as an emanation, but differing entirely from radio-active emanations.

All the properties ascertained identify the substance with hydrogen peroxide

Ordinary photographic dry-plates may be used to produce this effect ; care must be taken to select such as have been

preserved in wrapping materials themselves unable to act upon the plates.

The action takes place slowly at ordinary temperatures (one day to twenty-one days) according to the nature of the specimen, but rapidly at 50-55°C. (half to eighteen hours)

The shorter exposures give sharper pictures, which observation accords with the conclusion that the active body is of the nature of a vapour or volatile compound.

Bark and pith structure are almost inactive. Within the bark there is a bark-forming tissue, which gives alternate layers of active and inactive tissue. The latter was also found to have the property of being impervious to hydrogen peroxide.

The activity of the woods is increased in all cases by exposure to strong light, and observations on the spectrum showed that the blue end was particularly active.

The increased activity disappears on keeping the specimens after exposure in the dark.

Resinous substances extracted from a number of woods were found to be all more or less active. Para-abietic acid was prepared and found to be particularly active. It is well known that this body shows the phenomenon of autoxidation, which is no doubt associated with its unsaturated constitution.

The fossil resins show slight activity; coal also shows activity, and attempts were made to apply this to the indentification of different types of coal.

Woods were exhaustively treated with resin solvents, but were found to be still active, and the evidence goes to show that we are dealing with a definite property of the ligno-celluloses.

It is to be noted that a short exposure to steam or to chlorine gas renders the wood substance inactive.

The action is arrested in an atmosphere of carbonic gas, but is stimulated by the presence of oxygen.

Experiments in which the active substance in sufficient

mass was swept with a stream of air, and the current of air afterwards made to act upon a photographic plate at some distance, showed that the active substance could be carried forward.

It was also found that diaphragms carrying any substance capable of absorbing and destroying hydrogen peroxide arrested the action.

The investigation is still at this empirical stage. Russell has left an interesting legacy of highly suggestive observations, and the matter invites further investigation, as the exploration of the causes is calculated to throw a very important light on the natural chemical equilibrium of the ligno-celluloses.

The following communication is of importance as an exposition of the general perspective of autoxidation :—

ÜBER AUTOXYDATION ORGANISCHER VERBINDUNGEN.

H. Staudinger (' Chem. Ztg.,' 1911, 35, 1097).

This is a continuation and development of the critical investigations of C. Engler and J. Weissberg. Autoxidation of organic compounds is largely characterised by the addition of molecular oxygen at or to ethenoid groups : on the other hand the C : N group (Schiff bases) and N : N (as in azobenzene) are not autoxidisable nor is the ketonic CO group. Aldehydes do not react as

$$\begin{array}{ccc} & H & H \\ X \cdot CO + O:O = & X \cdot C & O \\ & & | & | \\ & & O\text{---}O \end{array}$$

but according to the equation

$$\begin{array}{ccc} O & O \\ X \cdot \ddot{C}H + O:O = X \cdot \ddot{C} \cdot O \cdot OH \end{array}$$

8
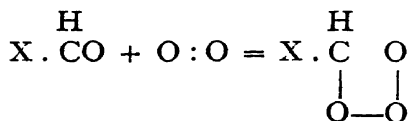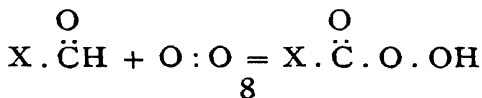
The reaction is comparable with that of benzoin formation and in fact those *aromatic aldehydes* only are autoxidisable which form benzoins, e.g. benzaldehyde and anisaldehyde; dimethyl amido-benzaldehyde on the other hand is inert. (Compare Baeyer and Villiger, ' Berl. Ber.,' 1900, 33, 1509.)

The following examples are typically characteristic of the influence of substitution on the autoxidation of the ethenoid grouping : $(C_6H_5)_2 = CO$. very oxidisable $(C_6H_5)_2 = CH_2$ feebly : $(C_6H_5)_2 = CCl_2$, $(C_6H_5)_2C = C(C_6H_5)_2$, and $CO = CH_2$ are inert.

The actual mechanism of the autoxidation is most clearly followed in the case of ethylenic compounds. The addition of oxygen to an ethenoid grouping may take the symmetrical form

$$\begin{array}{c} R_2C\!-\!CR_2 \\ |\quad\; | \\ O\!-\!O \end{array}$$
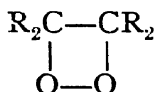
followed by resolution to

2 mol. $R_2C : O :$ or the asymmetrical

$$\begin{array}{c} R_2C\!-\!CR_2 \\ \diagdown\;\;\diagup \\ O : O \end{array}$$
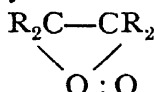
followed by loss of oxygen and production of an oxide

$$\begin{array}{c} R_2C\!-\!CR_2 \\ \diagdown\;\;\diagup \\ O \end{array}$$
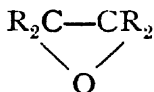
In the case of diphenyl ethylene the peroxide formed is very stable, but is quantitatively resolved on heating to benzophenon and formaldehyde :—

$$\begin{array}{c} (C_6H_5)_2C . CH_2 = (C_6H_5)_2C : O + CH_2 : O \\ |\qquad\; | \\ O\!-\!O \end{array}$$
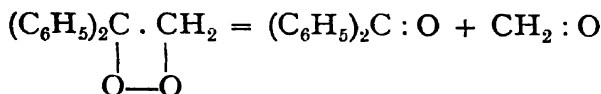
Similar addition and resolution produces from α chlorostyrol, benzoyl chloride and formaldehyde, and from phenylbutadien, cinnamic and formic aldehydes.

The highly oxidisable ketoketenes give characteristic results ; dimethyl and diethyl ketone react giving explosive oxides which are resolved into ketone and CO_2 thus

$$(C_2H_5)_2C \cdot \underset{\underset{O-O}{|\quad|}}{CO} \rightarrow (C_2H_5)_2C : O + CO_2$$
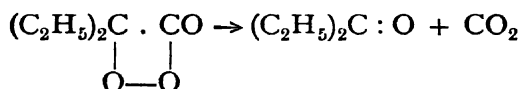
The general conclusion as to the mechanism of autoxidation is the production of the asymmetrical oxide as the first phase followed by rearrangement to the tetra-ring thus :—

$$R_2C \underset{\underset{O \,:\, O}{\diagdown\diagup}}{-CR_2} \rightarrow R_2C \underset{\underset{O-O}{|\quad|}}{-CR_2}$$
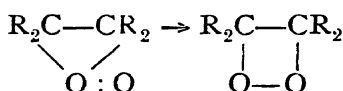
Both effects may thus be concurrent in certain cases, also the former phase may lead to the production of polymerides of the form

$$\left[(C_2H_5)_2C \underset{\underset{O}{\diagdown\diagup}}{-CO} \right]n.$$

* * * * * * * * * *
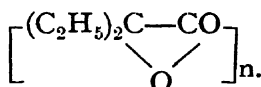
As we premised, these conclusions are in full accordance with our views of the constitution of the lignone complex together with the phenomena of autoxidation investigated by Russell. Molecular oxygen is fixed at the ethenoid linking as an asymmetrical moloxide ; one atom is split off, probably by interaction with 'constitutional' water, as hydrogen peroxide ; one atom remains combined as a tri-ring

$$-C \underset{\underset{O}{\diagdown\diagup}}{-C-}$$
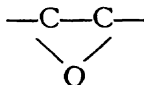
and accounts for the relative stability of the unsaturated groups of the lignone under ordinary conditions, that is in contact with atmospheric oxygen and moisture.

ABSORPTION OF PHLOROGLUCOL BY LIGNO-CELLULOSES, AND A METHOD OF QUANTITATIVE ESTIMATION.

C. F. Cross, E. J. Bevan, and J. F. Briggs ('Chem. Ztg.,' 1907, 31, 725).

THE COLOUR REACTIONS OF THE LIGNO-CELLULOSES

('Berl. Ber.,' 1907, 40, 3119).

* Of the numerous characteristic colour reactions of the ligno-celluloses, two have attracted special attention, since they are the basis of quantitative estimations of these compounds in mixture, more particularly of the proportion of 'mechanical' or ground wood in papers. These two reactions (*a*) with phloroglucinol in presence of hydrochloric acid, and (*b*) with dimethyl-p-phenylenediamine, are obviously in contrast and are typical of groups of reactions with phenols and with aromatic bases respectively.

In order to make use of these reactions in solving constitutional points, it is necessary to determine whether they are characteristic of the main complex, (ligno-cellulose) or of particular groups, or incidental by-products. We had already shown ('J. Chem. Soc.,' 1899, 95,752) that these colour reactions are affected, i.e. diminished, or even suppressed by certain treatments of the ligno-celluloses, without any constitutional change in the latter; it appeared therefore that the specific colour reactions may be due to by-products resulting from spontaneous changes within the complex, or determined by atmospheric oxygen, or moisture.

These suggestions are rather confirmed by the present investigation, of which the following are the main points :—

(*a*) *Reactions with phloroglucol*. The main reaction between the ligno-cellulose and the phenol is quantitative and independent of colour reaction ; the latter appears to be due

to a by-product and represents only a fraction of the total phenol combined synthetically.

(*b*) *Reaction with bases.* These reactions are not quantitative in the same sense as that with phenol. The colour reactions rather resemble dyeing processes, that is, the quantitative proportions are functions of the physical conditions of reaction.

(*a*) Interaction of phloroglucinol and ligno-cellulose. The general character of these reactions is indicated in the following comparative experiments :—

Equal weights of pure ground wood were treated (1) with 1 p.ct. of its weight of the phenol, and (2) with 10 p.ct. of the phenol in presence of aqueous hydrochloric acid (10 p.ct. HCl).

After ten hours' digestion in the cold, it was found that in (1) the phenol was entirely removed from solution, in (2) there was a considerable proportion residual.

The colour development in (1) was, however more intense than in (2).

The products were washed, dried, and weighed. The excess of weight of (2) over (1) amounted to 3·5 p.ct. This quantity indicates therefore a further combination with phenol, which can be calculated to represent 4·5 p.ct. of phloroglucinol, in which number no account is taken of water liberated in the reaction.

On these observations we conclude that there is a reaction in two directions, the first forming a colour derivative, and the limit of this reaction is at a point inferior to that represented by combination of the ligno-cellulose with 1 p.ct. of its weight of phloroglucinol.

The second reaction, which is a synthesis to a colourless compound of very considerable stability.

In order to make rapid quantitative observations on the influence of the varying conditions of reaction, a volumetric

method was devised based on quantitative combination of phloroglucol with either furfuraldehyde, or formaldehyde.

After a sufficient time for digestion under uniform conditions, the excess of the phenol is titrated by standard solutions of either aldehyde, using as indicator the colour reaction of the phenol, with the ligno-cellulose, ordinary 'news' printing paper being taken as test paper.

The details of this method are given in the second communication above cited.

The following numbers were determined for maximum absorption of the phenol calculated on the original ligno-cellulose, and without reference to further changes of weight attending the reaction. The numbers are therefore only approximate :—

Ground wood (coniferae) . .	6·71	6·63	
Jute fibre	4·23	4·26	4·34
Wood cellulose, sulphite process	0·75		
Esparto cellulose . . .	0·5		
Cotton cellulose . . .	0·2		

These numbers suffice to show that the quantitative method fulfils all requirements of a technical process of estimation of mechanical wood pulp, and are free from errors which are inseparable from the merely colorimetric estimation.

The results, however, are also useful in reference to problems of constitution, and the following determinations develop the observations from this point of view.

Two characteristic derivatives of the typical ligno-cellulose were treated under identical conditions with the following results :—

	Absorption of phloroglucol percentage of :—	
	Derivative	Original ligno-cellulose
Fully chlorinated jute, that is combined with 8 p.ct. of its weight chlorine .	3·9	4·0
Jute, acetylated to 29 p.ct. increase in weight	3·5	4·54

In both the above cases there was no colour reaction.

The results confirm the conclusion that the ligno-complex of jute is constitutionally unaffected by chlorination, as by acetylation ; the suppression of the colour reaction, especially in the acetylated product, is in accordance with a view that it is due to a by-product or grouping of furfural type, which group is acetylated at the position of a free CHO residue.

The main reaction appears to depend on the typical quinone group of the lignone, and this accords with the fact that it is not affected by chlorination.

It will also be noted from the figures p. 118 that the celluloses do not react, and the somewhat increased absorption in the case of wood and esparto celluloses may be referred to residues of lignone groups.

Since the celluloses in presence of hydrochloric acid tend to liberate aldehyde residues, it might be presumed that these would combine with the phenol. This supposition was negatived by observations on extreme products, of the so-called " hydro-cellulose " type obtained by the action of HCl gas.

	Maximum of absorbed phloroglucol
Hydro-cellulose cotton	0·42
Hydroligno-cellulose jute	4·45

(*b*) Reactions with bases. Aniline and its homologues, give characteristic colour reactions with the ligno-celluloses, the colours being modified by the introduction of negative groups ; thus, the aniline salts give a yellow reaction but the nitranilines give a red coloration, and the para compound has been suggested as a reagent useful in approximately estimating ligno-cellulose.

Of the diamines dimethyl-p-phenylenediamine gives the most striking colour reaction which was proposed by Wurster, and has been largely employed as the basis of a quantitative method of estimating ligno-celluloses. Wurster considered it due to active oxygen present in the ligno-cellulose, but the

effects are due to more complex causes ('Berl. Ber.,' 1886-87, 19, 3217; 20, 808).

The reaction with this base was carried out in the following series : four quantities of ground wood, each of one gram (air-dry), were treated respectively with 0·005, 0·01, 0·02, and 0·05, gram of hydrochloride, but dissolved in 20 c.c. of 5 p.ct. sodium acetate. At the same time a blank quantity was included. It was found that the intensity of the colouration in the series was proportional to the quantity of base.

After sixteen hours the four solutions all contained excess of base; on filtering and digestion with similar further quantities, the ligno-cellulose again developed coloration similarly proportional to the quantity of original base.

The coloured products after washing with water were analysed for proportion of nitrogen, the nitrogen being also determined in the blank quantity and deducted. The following table gives the results :—

P.ct of hydrochlorides taken	P ct. of nitrogen nxed in the product	Equivalent dimethyl-p-phenylenediamine
0·5	0·026	0·14
1·0	0·056	0·28
2·0	0·112	0·56
5·0	0·490	2·45

In respect of the above table, the figures are calculated to the basis of air-dry ligno-cellulose; for the percentages combined with actual ligno-cellulose they must be multiplied by the figure 1·1.

From these results it appears that the reaction of the ligno-celluloses with aromatic bases may be a reaction of the aldehydic sub-groups, or of associated aldehydic by-products.

In regard to the quantitative results, the reactions rather resemble reactions of 'adsorption,' as in dyeing processes.

There is an equilibrium of ligno-celluloses and bases in relation to the solvent medium, which is purely physical, that is, affected by mass, concentration, and temperature.

Phenylhydrazine.—This base while reacting similarly, differs with regard to its earlier phases, which show a total absorption of the base.   This is shown by the sub-joined figures.

P.ct. of phenylhydrazine in terms of ligno-cellulose	Absorption of phenylhydrazine
0·5	0·5
1·0	0·9
2·0	1·6
5·0	2·5

The constituent groups taking part in this reaction appear to be identical with those which combine with phloroglucol to give coloured products.   After reaction with phenylhydrazine, the phenol reacts very slowly, and evidently requires a first decomposition of the former compound (hydrazone) before reacting with the residue.

Generally the phenylhydrazine compounds, presumably phenylhydrazones, are more resistant than the colour derivatives obtained with simple monamine and diamine bases.   On the other hand, the phloroglucides are extremely resistant and not decomposed by boiling with aqueous alkaline solutions.

Hydroxylamine.—This base reacts, producing a change of colour which is a partial bleaching effect, and thereafter the ligno-cellulose does not react with aniline or diamines.

Further the phloroglucol reactions are modified in the sense that they only appear after some long period of contact.

UEBER DAS VORKOMMEN DER FORMYL-UND ACETYLGRUPPEN IM LIGNIN.

W. E. CROSS and B. TOLLENS ('J. F. Landw.,' 1911, 185).

Compare W. E. CROSS ('Berl. Ber.,' 43, 1526, and 'Dissertation,' Göttingen, 1910).

Of the various decompositions of the ligno-celluloses which yield acetic acid, destructive distillation is technically important as the main source of industrial acetic acid.   Other less com-

plex resolutions, chiefly alkaline and acid hydrolysis with and without oxidations, have been shown to yield acetic acid—as described in Cross and Bevan's ' Cellulose ' (1895). The authors have the opinion that the evidence so far available is not clear as to the identity of the actual parent groups in the lignone complex which thus break down to form acetic and also formic acid. They have therefore reinvestigated the matter by means of definitely simple hydrolytic treatments, as e.g. digestion with dilute sulphuric acid (1 p.ct. H_2SO_4) at 110°-130°. Typical lignocelluloses such as jute, beech wood, pine wood, and cereal straws yielded volatile acids calculated as acetic acid in the proportions 1·7-2·8 p.ct. of their weight. Formic acid was found always present, and in some cases was separately estimated.

Thus in the case of pine wood—in the form of ' ground wood pulp '—the yields were at 100°-115°

Formic acid   .   .   0·21 p.ct.
Acetic   ,,   .   .   1·06   ,,

that is, in the proportion 1 : 5 by weight. It was found on the other hand that other fatty acids higher in the series were not present.

The authors conclude that the results definitely confirm the view formulated by Cross and Bevan that ' lignin ' contains acetyl groups—as such. Formyl groups are also probably constituents of the complex, in addition to methoxyl, which is a constant of the various types of ligno-cellulose.

*   *   *   *   *   *   *   *   *   *

Upon this contribution we have only to remark that it is a careful and opportune confirmatory study, and especially in relation to such positive statements as ' das Fichtenholz-lignin ergiebt aber bei oxydation keine Essigsaure ' (Klason), which appear to require the specific and direct correction of the author's results.

The yield on oxidation is *a fortiori* higher than the yield from

processes of simple hydrolysis. Especially under acid treatment a limit is rapidly reached by interior condensations, and the lignone complex is very imperfectly resolved. The oxidation factor in many cases completes the resolution, and gives, therefore, the maximum yield of acetic acid.

To overlook the part played by acetyl and $CO . CH_2$ groups in the ligno-celluloses is not only to ignore prominent facts, but many important suggestions which they furnish towards the solution of the constitutional problem (see p. 103).

CHAPTER V

Technical developments. Brief notes of progressive developments of industries based upon the special chemistry of ' cellulose ' and derivatives. The following matters are dealt with, with illustrative special communications :—

Textile fibres, proximate composition in relation to spinning quality : cotton (flax and ramie), jute, and heart damage of commercial fibre.

Textile bleaches—chloramine reactions as incidental to processes of bleaching with hypochlorites, notably flax bleaches.

Ligno-celluloses and ' Rohfaser ' as constituents of cattle foodstuffs. The problem of digestion and assimilation.

Special cellulose industries. ' Artificial silks ' (lustra-celluloses) and the competitive evolution of the three processes of manufacture.

The viscose process and progress in production of ' silk,' and film by continuous process.

Cellulose Acetates: progress of industrial applications, with some considerations on technology of celluloid and technical conditions of competition.

TECHNICAL PROGRESS AND DEVELOPMENTS.

THE cellulose industries with their general and special technology are of colossal dimensions as object and subject of human activity. We make no attempt to chronicle or follow the lines of progress in so vast a field. We must in this section limit ourselves still more exclusively to impressionist sketches of matters which have come directly within our practical experience.

In the staple industries of textiles and paper-making we have noted the formation of specialist societies as an index of progress.

The Textile Institute was inaugurated at a meeting held on 22 April, 1910, at Manchester, of which a full account is contained in No. 1 of the 'T. I. Journal,' together with a list of original members. Of the first-fruits of this enterprise we signalise the following investigation on some constituents of raw cotton :—

SOME CONSTITUENTS OF RAW COTTON.
E. Knecht ('Textl. Inst. J.,' 1911, 2, 22-29).

Raw Egyptian cotton sliver was exhaustively extracted with benzene yielding 0·47 p.ct. of crude cotton wax, having the appearance and consistency of beeswax ('J. Soc. Chem. Ind.,' 1911, 813).

On treatment with petroleum spirit the crude wax was resolved into two constituents, cotton wax A, to the amount of about 70 p.ct. soluble in the spirit, and cotton wax B insoluble in petroleum. Cotton wax A has a pale colour, it melts at 66°-67°C., and consists for the most part of a true wax containing besides some free fatty acids, small proportions of glycerides, and some hydrocarbons.

Cotton wax B is a dark green, granular but plastic substance melting at 68°C. and containing very little free fatty acid. The Egyptian cotton deprived of wax yielded on extraction with alcohol 0·68 p.ct. of a solid extract, amorphous, very hygroscopic, and of a very rich brown colour.

Aqueous extraction which followed gave 1·46 p.ct. of a brown hygroscopic substance similar to the alcoholic extract.

Ammonia (25 p.ct. c.c. of a strong ammonia per litre) extracted 0·48 p.ct. Formic acid at similar dilution extracted 0·46 p.ct. of matter which was mainly mineral.

Texas cotton yielded 0·55 p.ct. of crude wax soluble in benzene ; the alcoholic extract amounted to 0·90 p.ct. and contained 1·07 p.ct. of nitrogen. It reduced Fehling's solution strongly. The aqueous extract was 1·61 p.ct., ammoniacal extract 0·39 p.ct.,

formic acid extract 0·72 p.ct.   The exhausted Texas cotton was digested with cold dilute hydrochloric acid, and yielded a further 0·43 p.ct. of extract.   Bengal cotton yielded only 0·38 p.ct. of crude wax.

Spinning trials were conducted on a large scale with the Egyptian cotton deprived of its wax.

The de-waxed cotton behaved very badly in the drawing and spinning processes, giving an excessive amount of waste irregular results, and showing a tendency to adhere to the rollers. Finer counts gave great trouble, and breakages were extremely frequent.   In the loom used as warp the de-waxed thread was also troublesome on account of breaks.

The yarn spun from de-waxed cotton was 24·5-27 p.ct. weaker than the ordinary yarn.   On the other hand, the extraction of the wax from ordinary yarn after spinning increased the strength by 13 p.ct.; the addition of 2 p.ct. of paraffin wax to this extracted yarn decreased its strength again by 33 p.ct.

J. Hubner has conducted dyeing experiments with the cloth manufactured from the de-waxed raw Egyptian cotton.

Substantive dye-stuffs gave lighter shades on the extracted cotton than on the ordinary.   Methylene blue and certain other dye-stuffs on the other hand dyed darker shades on the extracted cotton.

*   *   *   \+   *   *   *   *   *   *

This investigation, it will be admitted, breaks a long spell of indifference to questions of probably fundamental importance. We need not remind technologists that our leading textile industries are conspicuous cases of scientific evolution under the steady application of engineering and financial principles, and somewhat conspicuous for the neglect of the chemistry of the raw material.   The judgment of spinning quality by experience and empirical estimate is at least a 'fine art,' and so far justified by practical results and industrial success on a colossal scale. But it can hardly be presumed that the factors of composition

of raw cotton are without ascertainable influence on spinning quality. The results of preliminary investigation above recorded make out a strong case for the contrary, or for the positive doctrine that spinning quality is definitely related to the proximate composition of the fibre substance. If this proposition, which would appear to be self-evident and of general import, had been applied to fibres such as flax and ramie, we should have been saved many costly failures of systems of separating and preparing these fibres for the spinner. 'Artificial' processes of flax retting, and chemical treatments of rhea or rhea bast ribands for the separation of the fibres, affect the non-cellulose components of the fibres more or less profoundly ; and *pari passu* with the removal of these or with modifications of their properties, there is a loss of spinning or drawing quality.

Repeated failures of would-be pioneers of 'improved' methods have no doubt confirmed the prejudices of those trained in the traditions of empiricism. But critical study of many of the suggested improvements shows that they are equally empirical in conception and aim, and our industrial leaders must admit that a revision of standard processes in the light of first principles may yet disclose potentialities of unrealised developments. These are suggested in the history of invention and its failures; and it is evident that failure is not the last word of a movement unless the causes can be critically referred to first principles.

The work of the Textile Institute will no doubt help to secure a general recognition of such principles as define the relations of the spinning processes to minute structure of the spinning units or 'elements' on the one hand, and the composition of the complex mixture which constitutes the fibre substance on the other.

The *jute fibre* presents a type of structure and composition obviously very different from flax and rhea, which are also bast fibres, and still more divergent from cotton. The jute industry, therefore, presents a special group of problems, though

of the same general character.   An exceptional problem is one connected with the conditions of handling and transporting the raw fibre.   Commercial bales of jute shipped from India to European textile centres are liable to a depreciation of quality which in extreme forms is known as 'Heart Damage'.   This is a disintegration of the fibre substance observed for the most part at the centre of the bales, and which observation has connected with the influence of moisture, but obviously, as a fundamental condition, with the chemical sensitiveness of the fibre substance.

We have recently carried out direct investigations of the problem of the immediate causes of the phenomena, and we reproduce our report which as a Government document is not generally accessible to students of technology.

REPORT BY MESSRS. CROSS AND BEVAN ON INVESTIGA-TIONS OF JUTE FIBRE IN RELATION TO HEART DAMAGE OF BALED JUTE.

Following the appointment of Mr. Finlow as expert adviser on fibres to the Government of Eastern Bengal and Assam, we were asked by him to express an opinion as to 'normal moisture' of jute fibre.   Our correspondence on the subject dates from January, 1907.

In our correspondence the question was raised incidentally, whether excessive moisture in packing, i.e. baling, could lead to damage to fibre, and particularly to the damage known as 'heart damage'.   In its extreme form this damage represents total disintegration of the fibre, which breaks down under slight pressure to a fine dust.   When it occurs it is usually found at the centre of the mass of the commercial bales of fibre.

We suggested that an investigation might enable us to fix the cause of this phenomenon, or at least narrow the problem to very definite issues, and permission was given to undertake the work, on behalf of the Government Department, in collaboration with Mr. Finlow.

As a preliminary to the account of the results obtained, we make a few general observations on the subject-matter.

Jute, as a staple textile fibre, has its special and obvious interest, and we need only refer any outside readers to the articles ' Corchorus ' and ' Jute ' in the ' Dictionary of Economic Products of India,' vols. ii. and iv. (George Watt). These volumes, published in 1889-90, are followed by the ' Agricultural Ledger,' of which No. 37 (1896) is particularly relevant, as it contains reports on methods of harvesting jute, and preparing it for the market, and more particularly contains the results of examination in the Research Department of the Imperial Institute of specimens of the fibre experimentally grown and treated (1) with a view to ascertaining the best period for harvesting jute so as to secure the highest quality of fibre, and (2) to discover a means of protecting the fibre against fermentation and other changes to which it is liable during transport.

We have been concerned in suggesting some of these practical researches, and there is a certain continuity of ideas connecting these investigations with those about to be described.

The jute fibre has also a peculiar scientific interest as a chemical type ; it is, in fact, the representative ligno-cellulose, and from this point of view has occupied us, as a matter of research, since the year 1880.

In addition to the pure chemistry of this ligno-cellulose, we have given some attention to the question of its growth and elaboration in the plant, for which investigation we carried out cultural experiments in this country, separating the bast fibre and submitting it to chemical investigation (see ' J. Chem. Soc.,' 1893-94, v. 63, 964 and v. 65, 470).

It is important to bear in mind that what is established for the typical ligno-cellulose has a general bearing on this diversified and economically valuable group of vegetable products ;

also that the phenomena of destruction of fibre, obviously un-desirable in the case of jute, may become a most desirable process, under control, for the utilisation of lignified 'waste' or by-products, such as wood sawdust, cereal straws, etc. etc.

Our more special investigations, with those of other workers who have contributed, are summarised and discussed in our publications, 'Cellulose'[1] and 'Researches on Cellulose, I. and II.' We make this reference to preceding literature since, in dealing with the present aspect of the matter, we must employ the scientific terminology as well as presume a general acquaintance with the science of the subject.

For the purposes of our present inquiry, the main features of the composition of this ligno-cellulose may be stated in terms of the products of its more characteristic resolutions.

Cellulose.—Cellulose (*a*) similar to cotton cellulose. Cellulose (*b*) yielding furfural and containing OCH_3 groups ; more sensitive to action of hydrolytic agents.

Non-Cellulose.—Lignone, quinonoid complex, characterised more particularly by direct combination with chlorine to a derivative of formula $C_{19}H_{18}Cl_4O_9$; resolved by oxidants under hydrolytic conditions, chiefly into acids of low molecular weight.

Neither the cellulose nor the non-cellulose are homogeneous. Although in the chlorination reaction they maintain their integrity, the distinctive features of the group in this reaction are sharply contrasted, and when followed by the action of solvents, and more especially sulphite of soda, their resolution is sharp ; the cellulose resisting, and the non-cellulose complex passing into solution.

Under the action of other re-agents, the complexity of the groups is shown by various resolutions, of which characteristic products are, furfural (boiling with hydrochloric acid), methyl iodide (boiling with hydriodic acid), derived from and quanti-

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[1] Longmans, London, 1895-1905.

tatively measuring methoxyl, acetic acid (all simple hydrolytic resolutions).

But the study of these is not yet sufficiently exhaustive to enable us to integrate the products into a definite constitutional formula or diagram of composition of the fibre substance.

One point may be noted, that the non-cellulose complex is related to the benzenoid group of unsaturated compounds, and stands in probable genetic relationship to the tannins, or more generally the phenolic constituents of plant tissue. It must also be noted that jute as a ligno-cellulose is a prototype of the substance of ligneous or woody tissue, which, though occurring in enormous diversity of structural forms, is exceptionally uniform in regard to chemical type. With the ground tissue of the woods are often associated characteristic 'aromatic' compounds, which may be aromatic in the ordinary sense (such as vanillin) or may be colouring matters (hæmatoxylin, quercitrin, etc.), or tannins, which have considerable chromogenic properties.

It is probable that transitions from the ligno-cellulose to such derivatives take place in the normal course of plant life, but the mechanism of such transitions has not been elucidated. We mention this section of plant physiology in connection with our earliest investigation of a specimen of damaged jute, i.e. jute which had undergone disintegration in the centre of a commercial bale of fibre (see 'J. Chem. Soc.' 41 (1882), 92-93). The disintegrated fibre on treatment with water gave an astringent solution which gave colour reactions with iron salts and copious precipitations with gelatin.

These are the reactions of the tannins. To establish the identity more positively, the solution was treated for the isolation of its main components, which proved to be a tannin-like substance of formula $C_{23}H_{24}O_{16}$ and a strongly acid body separated as barium salt $C_{29}H_{24}O_{29}Ba_2$ which was a 'saturated'

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compound, and probably derived from an original carbohydrate constituent of the fibre.

The low percentages of cellulose isolated from these specimens, viz. : 57·0, 58·5, 64·0, 66·0, show that the attack had affected the entire ligno-cellulose.

Specimens of the ordinary 'heart damage,' i.e. fibre which has suffered disintegration at or near the centre of the jute bales of commerce, have been recently examined by us in connection with this investigation.   For the selection and supply of typical specimens we are indebted to Messrs. Ide and Christie and Mr. G. C. Keiller, Secretary of the Dundee Chamber of Commerce.   But the results are in certain aspects in direct contrast to the above.   Though showing a considerable proportion of water-soluble constituents, these contained no tannins, but consisted rather of carbohydrate derivatives.

The description of these bodies is contained in the subjoined general account of the proximate composition of the damaged fibre, and it will be seen that the divergences from the normal result from decompositions of a somewhat different order.

In fact, the divergences of the products of resolution in regard to fundamental chemical constituents are small, although the proximate condition of the fibre substance is very widely different from the normal.

On a particular specimen, representing the disintegration in its extreme phases, we made the following observations :—

(*a*) Normal fibre of same bale (in fact, from same strands as (*b*)).

(*b*) Damaged disintegrated fibre, resolved into a fibrous powder by dry rubbing through a sieve.

	(a)	(b)
Moisture . . .	10·7	9·8
Ash	1·2	1·3
Constituents soluble in water .	1·1	11·5
Soluble on boiling with 1 p.ct. NaOH .	11·0	23·3 (5 mins. boiling)
	14·0	58·3 (60 mins. boiling)
Furfural (total)	7·8	5·8
Phloroglucol absorption	4·2	8·0
Chlorination reaction (HCl formed) .	8·0	10·2
Cellulose (after dissolving chlorinated derivative)	75·0	62·6

These are the more characteristic 'constants' of the ligno-cellulose, for the full discussion of which the special literature previously cited must be consulted. The following points are to be noted :—

Water-soluble Components.—The large proportion of these is significant of the deep-seated attack, but more significant are their group characterisations. The reduction of cupric oxide (Fehling's solution) is equivalent to that of 26·0 p.ct. glucose calculated to the total dissolved solids. After boiling with dilute acid, the reduction was increased to 44·8 p.ct. (on the same basis). We have already noticed the absence of aromatic products and the contrast in this respect to the case previously investigated.

Reaction with Phenylhydrazine.—The solution reacts directly in the cold : a brownish-red body is precipitated which appears to be an osazone. It crystallises from benzene. The yield from a 1·2 p.ct. solution of the solids was 0·31 gram per 100 c.c.

After inversion (boiling 2 p.ct. H_2SO_4) the yield of osazone precipitated in the cold was decreased to 0·2 per 100 c.c.

On filtering from the product formed in the cold and heating to 95°C. a further production of osazone was determined, amounting to 0·3 gram per 100 c.c.

Preparations of these derivatives are under investigation with a view to determine the molecular formula of the parent compounds (see supplementary report, p. 149). The direct

reaction with phenylhydrazine in the cold, suggests the presence of a body containing two CO groups in the 1·2 position, i.e. an α diketone or ketoaldehyde as a main constituent of the mixture, the formation of which represents a total hydrolysis of the lignone complex. The osazone produced in the filtrate on heating has the characteristics of a glucosazone, and the production of a glucose or C_6 sugar would appear to indicate an advanced hydrolysis of the cellulose, only requiring the action of dilute acid to render complete. These are the most important points to note in elucidation of the general character of the resolution.

Furfural Constant.—The reduction of furfural below the normal is due to one of two causes, either (1) the 'furfuroids' have been specifically attacked, i.e. selectively assimilated by an organism, or (2) they have been constitutionally modified, as e.g. by deoxidising or reducing actions of associated groups of the complex.

This introduces a somewhat controversial point. It is often assumed that these furfural-yielding compounds are pentoses, or C_5 sugars (or their anhydrides). But since condensation to furfural or furfural derivates is a property of certain hexoses and their oxidised derivatives, it is not legitimate to adopt the limitation a priori.

In this particular case the general conclusion to be drawn from the determinations of furfural, is that the attendant conditions of hydrolytic change of the ligno-cellulose have been those of deoxidation or reduction. The converse would certainly hold, that oxidation of the fibre substance increases the furfural.

The pentoses or pentosanes are relatively resistant to ferment actions, and it is difficult to see how the typical CO group of a pentose can have undergone a reduction, as, for instance, to a CHOH, or CH_2OH group.

Oxyhexoses, on the other hand, would be less stable, and

more liable to constitutional change affecting their conversion into furfural. Leaving this point open, we consider the conclusion so far warranted that diminution of furfural is an indication that the oxygen equilibrium of the ligno-cellulose has been affected, in one of the many ways which we may assume to characterise the attack of anærobic organisms.

These observations have been confirmed by observations on other samples of heart-damaged fibre. In one specimen we determined :—

		Furfural Yield
In damaged fibre (fine powder) . .	.	6·4 p.ct.
In normal fibre of same strands .	.	8·2 ,,

This specimen also, on boiling with dilute soda (1 p.ct. NaOH) for one hour, showed a loss of 56.7 p.ct. as against 12·4 for the normal.

Phloroglucol Absorption.—This reaction and the resulting ' constants of absorption ' have recently been investigated by the authors and J. F. Briggs (' Ber. Deutsch. Chem. Ges. ' 1907, 3119). In a series of ligno-celluloses it is a measure of lignification, i.e. of the relative proportion of lignone groups. It is a specific characteristic of these groups as compared with cellulose, which does not react.

The increased reaction with this phenol would appear to indicate a relative increase of lignone at the expense of other groups. But it may also be explained as resulting from liberation of CO groups of the lignone complex from union in condensation with other groups, which, in the normal state, oppose the condensation with the phenol. The constitutional features of the water-soluble compounds favour this view. Moreover, they are observed to react directly with the phenol.

The following further observations on this reaction may be noted.

The second sample of damaged fibre gave the following results :—

Phloroglucol absorbed

Damaged fibre   .   .   .   .   . 6·9 p.ct.
Normal fibre (same strands) .   .   • 4·3 ,,

Chlorination Reaction.—This follows its ordinary course and affords an important index that the general constitutional features of the ligno-cellulose complex are maintained side by side with deep-seated proximate modifications.

The production of acid (HCl) which attends the chlorination is rather higher than the normal, indicating that the fibre is in a more oxidisable condition.

The isolation of cellulose by the usual method of dissolving away the chlorinated complex, is of course affected by the sensitiveness of the modified cellulose to alkaline hydrolysis, and we need only attach a general value or significance to the numbers for cellulose. They, however, certainly indicate the very considerable constitutional changes which have accompanied the structural break-down of the fibre.

It is important to note that the disintegration is similar in character (microscopically) to that determined by acids, that is, the fibre bundles are attacked integrally. and there is no tendency to resolution of the bundles into constituent ultimate fibres.

These constants define the changes in constitution of the fibre substance, which accompanies the 'heart damage' of the bales, and are, no doubt, sufficiently characteristic to be applied to diagnose the earlier or intermediate stages of destruction.

The observations lead to the following general conclusions :—

The decomposition affects the entire ligno-cellulose complex and the cellulose as much as the lignone components. The main feature is a far-reaching hydrolysis, which in general resembles the attack of strong hydrolysing acids ; the secondary features are rather those of deoxidation.

The resolved complex is in a highly reactive condition due

to the liberation of the CO groups (reactions with Fehling's solution—phenylhydrazine) and is a perfect nutrient medium for micro-organisms of all kinds ; the aqueous extract inoculated with mucor showed a copious growth after forty-eight hours' incubation.

It was evident from the microscopic examination of the fibre that the mould growths which were present were external to the fibre bundles, and their disintegration could not be attributed to penetration by the mycelia of the moulds. The conversion of so large a proportion of the fibre substance into fully hydrolysed and assimilable or nutrient matter is suggestive, on the other hand, of enzyme action, and our general conclusion is that the destruction of the fibre is the result of bacterial and other organisms developing under anærobic conditions.

We need hardly insist that we do not regard the evidence thus summarised as complete ; but it supplies a general conclusion serving as a definite working hypothesis to guide us in our investigations. The inquiry must be pursued for the accumulation of the much greater weight of evidence necessary for precise definition of the phenomena.

On this hypothesis we have, in connection with Mr. Finlow, carried out an investigation the scope of which is implied in the following account of the experiments and their results.

From a uniform large quantity of commercial fibre, six quantities of about $2\frac{3}{4}$ cwt. each, were selected and put up into bales with addition of water to bring the total moisture up to 25 to 30 p.ct i.e. with addition of 15 p.ct. water in each case.

This was considered to be a maximum proportion, i.e. meeting the extreme possibilities attending the baling of the fibre.

A. One of these, serving as a blank, was put up with the *added water applied only*, by means of a special spraying apparatus, and the others were treated as follows :—

B. With the water was added 30 grams mercuric chloride previously dissolved in the water and sprayed as in A.

C. With the water 350 grams of pure formaldehyde taken in the form of commercial formalin of 40 p.ct. strength (875 grams).

D. With the water 1,156 grams cane sugar.

E. Water and sugar as in D, with 35 grams mercuric chloride in solution.

F. Water and sugar as in D, with 350 grams pure formaldehyde.

These bales were shipped to London in the ordinary way and on arrival were at once cleared by Messrs. Cook & Co., and laid out for inspection at their warehouses.

The bales were opened on 27th January in the presence of Mr. Ide (Messrs. Ide & Christie), and of a deputation of experts, including Mr. C. Ritchie, Mr. W. Polson, Mr. F. C. Sheppey, also Colonel D. Pitcher, R.E., of the Imperial Institute Advisory Committee, and two of the technical staff of the Institute, Dr. Goulding and Mr. Ladell. We take this opportunity of acknowledging the active interest taken by the London Jute Association, through Mr. C. Barber, Secretary ; the Dundee Chamber of Commerce, through Mr. G. Keiller, Secretary ; and on the scientific side of the investigation by the Imperial Institute, through Professor Wyndham R. Dunstan, F.R.S.

The experts made a careful examination of the bales, and their judgment is recorded in the written reports kindly furnished by Mr. Ide, Mr. W. Polson of W. F. Malcolm & Co., 36 Leadenhall Street, E.C., and Mr. F. C. Sheppey, on behalf of the London Jute Association, 24 Mark Lane, E.C., as follows :—

THE LONDON JUTE ASSOCIATION.

Mr. F. C. Sheppey's Notes.

Six bales of jute examined at Creechurch Lane Showrooms, 27th January, 1908.

'In my opinion no result of practical value can be deduced from the experiments made with these bales, chiefly because they are not of the ordinary weight (being only about 2½ cwts. each) and were not subjected to the usual heavy pressure in packing, which would largely affect the liability of the fibre to weaken and deteriorate in consequence of dampness.

'The following are some notes of my examination :—

'Series I.
　'*Bale A.*—The fibre appears strong and glossy, but upon examination the jute is damp and not so strong.
　'*Bale B.*—Similar in appearance to A, but drier and stronger.
　'*Bale C.*—Very similar to bale A.
'Series II.　(Treatment as per Messrs. Cross and Bevan's advice.)
　'*Bale D.*—Does not feel so damp as A, but is otherwise similar in appearance and strength.
　'*Bale E.*—This bale is the least satisfactory in appearance, the fibre seems dull, and a good deal of jute is decidedly weak.
　'*Bale F.*—This jute feels very damp, but it had retained excellent strength.
'The general quality and colour of the jute is satisfactory and does not call for any comment.'

NOTES OF MR. IDE, OF MESSRS. IDE AND CHRISTIE.

Messrs. Cross and Bevan.

' Gentlemen,

　'With regard to the six bales Bengal jute examined with you, we have to say the quality was of a superior class ; all was more or less damp in a slight degree, but not sufficiently so to cause difficulty in selling to the consumer with whom we placed the parcel.'

MEMORANDUM FROM W. F. MALCOLM & CO., TO MESSRS.
CROSS AND BEVAN.

Six Bales of Jute at Creechurch Lane.
27th January, 1908.

'All six bales appear to be the same general type of jute, and probably from the same original pile.

'The colour of all six for October shipment is normal.

'Series I.

'*Bale A.*—Feels damp, but is otherwise in good condition, and about normal strength for October shipment. .

'*Bale B.*—Freer from damp than A, and rather stronger.

'*Bale C.*—Strength as in A.

'Series II.

'*Bale D.*—Fairly dry to the feel, has not suffered in appearance, but fibre is not so strong as it looks, and is in this respect rather below normal.

'*Bale E.*—Weaker than D, both in appearance and reality.

'*Bale F.*—Feels very damp, but strength has apparently not suffered meantime.

'W. N. POLSON.'

Our own conclusions from the inspection were that there were indications of attack on the fibre in certain cases, especially in the blank A, and the fibre containing added sugar D; the two specimens containing formalin, C and F, appeared normal; B and E were intermediate. Temperature observations were made and disclosed no tendency to heating.

Average samples in two series, I. and II., were drawn from the bales, and immediately transferred to stoppered bottles; those required for bacteriological examination being placed in sterilised bottles.

Series I.—On examination in the laboratory, we obtained

the following numbers for (1) moisture, and (2) matters soluble in water :—

(1) *Moisture.*—The weighed samples were air-dried, and the losses noted ; (*a*) the air-dry fibre was further dried at 100°, and the further loss estimated (*b*).

(2) *Soluble Matters.*—The sample was boiled for five minutes in distilled water.

	Moisture			Water Soluble Matters
	(a)	(b)	Total	
				P.ct.
Bale A.	10·4	11·9	22·3	1·10
„ B.	10·2	11·8	22·0	0·73
„ C.	8·2	17·9	26·1	0·88
Containing the added sugar . . D.	5·6	10·8	16·4	2·10
E.	7·2	13·6	20·8	2·40
F.	12·3	13·2	25·5	2·8

We made further examinations of particular samples as follows :—

Sample D was examined to determine the condition of the sugar, which had been originally added as cane sugar. Three-quarters of the sugar was still in the condition of cane sugar ; one-quarter had been inverted to 'reducing' sugars.

Samples C and F were examined for formaldehyde, which was found to be present in the free state.

These results are evidence of the accuracy with which the programme of the special treatments have been carried out, and the efficiency of the methods adopted, as well as of the antiseptic treatment devised, and as regards the special points under investigation (1) that the excess of moisture added as described had been very satisfactorily retained ; and (2) that no marked constitutional changes in the fibre substance were yet in progress.

A further confirmation of these conclusions was that the fibre, subsequently sold in the open market, realised the figure of £23 10s. per ton. The results are a certain tribute to the resisting qualities of the ligno-cellulose, but the experts consider that the small size and relative bulk of the bales must be taken into account in drawing conclusions applicable to the fibre under the conditions of the ordinary commercial bale. In further elucidation of the special points under investigation, we made a further series of observations upon the samples.

Having failed to bring about any material development of organisms under the conditions described, we exposed average samples to the direct test of incubation in a moist atmosphere, i.e. under aerobic conditions, at 35°C.

The following observations were made upon the samples thus incubated :—

Incubation Period	A	B	C	D	E	F
27 Jan. 0 days	—	—	—	—	—	—
3 Feb. 7 days	Strong smell	'Earthy' smell	Slightly 'sour'	Strong acid smell (butyric)	No smell	No smell
14 Feb. 18 days	Smell of farmyard manure	Slight, sour	Slight	Very strong sour smell	Sweet	Sweet
6 Mar. 40 days	Mouldy; fibre much blackened and weakened	Slight earthy, fibre reddish, no lustre	Sweet, fibre bright	'Earthy' smell, fibre yellow and weak	Earthy smell, lustre inferior, colour reddish	Sweet, fibre bright, and colour good

It appears from the above that considerable mould and bacterial growth resulted from the 'blank' samples. They were in large part inhibited by the mercuric chloride, and entirely by the formalin.

The weakening of the fibre in A and D was pronounced. We further examined certain of the samples with the following results :—

Loss of weight by alkaline hydrolysis—

				Before incubation				After incubation
A.	.	.	.	10·1	.	.	.	12·0
F.	.	.	.	7·9	.	.	.	7·4

This shows that the attack on the ligno-cellulose was of a very different order from that which characterises ' heart damage '.

The general conclusion to be drawn is that formaldehyde is a very efficient protecting agent, and we have reason to think that it may act not merely as an antiseptic, but in virtue of reacting positively with the ligno-cellulose.

In regard to the general question of the growth of organisms at the expense of the fibre substance, the question arises as to the supply of nitrogenous nutrient matter.

The total nitrogen in a mixed sample of the fibre A-F was estimated at 0·16 p.ct. We have also estimated the nitrogen in ' heart-damaged ' fibre, and the normal fibre of the same bale, which we found to be :—

Normal fibre	Damaged fibre
0·155 p.ct.	0·156 p.ct.

The nitrogenous residues of the tissue parenchyma appear, therefore, to have no determining influence, though on general grounds a necessary associated cause.

These results are important. The reactions obtained are, of course, those of organisms growing under *aerobic* conditions, and although the destruction of the fibre in A and D was well marked, there was only a slight change in the composition of the fibre substance.

Thus, the following numbers were obtained for percentages of soluble components in the ' blank ' untreated fibre :—

A. Percentage soluble matter in specimen after six weeks' incubation at 35°C., 1·2 p.ct.

Which shows the absence of any hydrolytic changes such as mark the destruction of the fibre by 'heart damage'.

Series II.—Bacteriological Tests of Fibre of experimental Bales.—A sample of the fibre was drawn from the centre of each bale and transferred to a stoppered bottle previously sterilised; the samples were submitted to bacteriological examination.

The culture experiments were performed on infusions made by treating the jute with sterilised water. It must be observed, in regard to the results which are given below, that the samples were drawn in the warehouse filled with the fibre dust usually found in such places, and our precautions may have been insufficient to prevent infection.

Plate Cultures.—These were carried out with agar-agar and incubated at 35°C.; examinations were made from day to day, and the results finally taken after five days.

A. Many colonies which had liquefied.

B. The medium contained several moulds and colonies of bacilli, non-liquefying.

C. Many liquefying organisms.

D. Colonies, bacilli, non-liquefying.

E. Showed only a single colony of spore-forming coccus.

F. Same as E.

Microscopic Examination of Colonies.

A. Showed bacilli only.

B. Bacteria and mould spores.

C. Bacteria and cocci.

D. Bacteria only.

E. Mould spores only.

F. Same as E.

We attach importance to the results with samples E and F,

showing that in these cases the fibre had been practically steril-ised by the treatments. The differential comparisons which should be established by these observations must be instituted with the reserve imposed by the samples having to be drawn in a dust-laden atmosphere.

We have now to set out briefly the issues of this investiga-tion.

As its purpose was to contribute in a practical way to in-dustrial problems we will give precedence to the points of ' practical' moment.

1. It is shown that jute will hold and retain excessive mois-ture (25 p.ct.) under ordinary conditions of transport and storage, even when baled in relatively 'light' bales.

2. This excessive moisture *per se* causes no evident damage nor lowering of the quality of the fibre.

3. The presence of easily fermentable matter associated with excessive moisture, does not constitute a combination necessarily dangerous to the fibre.

4. Mould and bacterial growth may develop on the fibre without causing deep-seated changes of the fibre substance.

5. The specific chemical features of 'heart damage' are profound changes in the fibre substance as a complex without correspondingly large changes in the constitution of the proxi-mate constitutent groups.

6. There are definite suggestions that the particular condi-tions determining these changes are (*a*) enzymic action resulting from the growth of organisms under (*b*) anaerobic conditions.

7. It is shown that formaldehyde in economical proportion is an efficient preservative and generally inhibits the growth of micro-organisms in masses of the fibre.

We now point the *scientific results* of the investigation, necessarily incomplete, and therefore, in part, in the form of hypotheses, which however are definite.

1. The chemical constants of the heart-damaged fibre are

specific, and their application in the systematic examination of the fibre under various conditions of storage, should lead to the diagnosis of the changes in their incipient or earlier stages, and thus to the more rapid determination of the actual operating causes.

2. 'Heart-damaged' jute represents a reversion of the ligno-cellulose to a condition which we may assume to represent some of the phases of progressive elaboration in the growing plant. The conversion of the ligno-cellulose into hydrolysed and therefore nutrient or assimilable matter available for living organisms, is an important object of research in agricultural chemistry, and the investigation of heart-damaged jute may furnish results of positive economic value to other industries.

3. A further confirmation is afforded of conclusions from purely chemical evidence that a 'ligno-cellulose' is not a *mixture* of a normal cellulose and lignone groups, but a complex in which the union is of a more intimate order, and which is not resolved by profound hydrolytic changes. Both the 'saturated' (cellulose) and 'unsaturated' (lignone) constituent groups of the ligno-cellulose are attacked *pari passu*, and the general features of 'heart damage' is hydrolytic action under deoxidising or perhaps non-oxidising conditions.

It is evident that a considerable extension of these investigations is called for, and that there are prospective results of value to be attained. We make our suggestions as follows :—

1. *Formalin treatment.*—In view of the sensitiveness of the jute fibre substance to natural destructive agencies, of which 'heart damage' is an extreme manifestation, it is a matter of moment to test the general value of a formalin treatment on the lines herein disclosed.

The proportion of 14 lb. commercial formalin per ton of fibre, representing a value of 5s. at the outside, has been shown to be a maximum for the purpose of arresting growth of organisms in the baled fibre.

It appears worth while to test such a treatment on a practical and commercial scale. The formaldehyde may have a double function in this case, not merely antagonising the growth of organisms, but influencing the fibre substance by chemical action, and particularly rendering it less sensitive to hydrolytic agencies.

The observations in this direction should, of course, be carried out progressively and with due caution.

Should the department adopt this suggestion it is obvious that Mr. Finlow is already in possession of the practical methods of carrying out the treatment.

We would suggest as a point in the economic application of the formalin, that the proportion of 7 to 14 lbs. per ton of fibre is already indicated as sufficient, varied between these limits according to the quality of the fibre; further, that by reason of the volatility of the formalin it may be applied in relatively larger proportion to the fibre making up the centre of the bale. From the centre it may be expected to diffuse outwards and distribute itself more or less uniformly in the long period which elapses before the fibre is worked up in the European factories.

We make the suggestion in these general terms, holding ourselves at the disposal of the Government for co-operation in the observations necessary to test the practical value of the treatment.

2. *Co-operative investigation.*—In following up these investigations it appears to us that a systematic programme of experiments and researches should be carried through as follows :—

(a) *To reproduce the phenomena of heart damage.*—This is evidently the issue of precise general knowledge of the operative causes, and of these we require to establish the actions of particular organisms or groups of

organisms, and whether specific conditions are necessarily associated. The bales of normal fibre should be ' incubated' at 30-35°C., the same with excess of moisture, the same with portions of heart-damaged fibre put up with the normal fibre. These experiments should be parallel with observations on masses of fibre sufficiently loose to allow access of air.

(*b*) To accumulate information with regard to heart damage, by investigating the cases which occur as completely as possible.

(*c*) To make general observations on commercial jute to determine the actual changes, if any, of the normal fibre as a normal result of remaining several weeks or months in the commercial bales. For this purpose, *close comparative chemical examination of fibre drawn* from the bale, and the same fibre sampled at the time of baling, and sent over in the form of a loose package.

In such investigations we suggest the jute trade would gladly co-operate, and if this could be secured by proper representation of the advantages to result, we have little doubt that the scientific side of the work could be adequately provided for, through the institutions already existing, with the collaboration of those who, like ourselves, have a special interest in this aspect of the matter.

Should the Government decide to give effect to these recommendations in any way, we offer our services in collaboration with others whose valuable services could be impressed. The subject is one of widely varied importance, and we suggest, outside the range of adequate appeal to private interests, eminently, therefore, a matter requiring the organising influence of a Government Department.

CROSS AND BEVAN.

The following are the results of elementary analyses of normal and heart-damaged jute, and products of the latter :—

1. Normal fibre from sound portion of strands—

    0.1390 gave 0.2114 CO_2, 0.0811 H_2O.
    Residual ash, 0.0005.
    Correcting for moisture (9.8 p.ct.) and ash.

Carbon	.	.	.	.	.	.	46·2
Hydrogen	.	.	.	.	.	.	5·4
Oxygen	.	.	.	.	.	.	48·4
							100·00

2. Heart-damaged fibre in fine powder—

    0.1861 gave 0.2782 CO_2 and 0.1067 H_2O.
    Residual ash, 0.0042.
    Correcting for moisture (10.4 p.ct.) and ash.

Carbon	.	.	.	.	.	.	46·7
Hydrogen	.	.	.	.	.	.	5·4
Oxygen	.	.	.	.	.	.	47·9
							100·00

It is evident from these comparative figures that the profound changes in the fibre substance accompanying heart damage are such as to leave its ultimate or elementary composition unaffected.

Water Soluble Components of Heart Damaged Fibre—
Phenylhydrazine Derivatives.

Preparation A.—The aqueous extract was filtered, acidified with sulphuric acid, filtered from a flocculent brown-coloured precipitate, and treated with phenylhydrazine acetate in presence of excess of sodium acetate.

A copious precipitate of bright orange yellow resulted, which was washed, dried, and analysed.

(*a*) o·1229 gave o·2642 CO_2 and o·624 H_2O.

(*b*) o·1094 gave 11·2 c.c. N at 23° and 718 mm.

Calculated for $C_{24}H_{28}N_4O_8$.

Hence—

(*a*) Carbon	.	.	.	.	.	.	58·5	57·6
Hydrogen		.	.	.	.	.	5·6	5·6
(*b*) Nitrogen .		.	.	.	.	.	11·1	11·2

This body has all the characteristics of the osazones, and being produced by reaction in the cold, the evidence indicates that the parent substance is a body $C_{12}H_{14}O_{10}$ with two constituent CO groups in contiguous position. But to establish this conclusion it is obvious that an extended investigation is necessary.

Preparations B.—The aqueous extract was treated as above, but heated for two hours at 98° in presence of sulphuric acid (2 p.ct. H_2SO_4).

Acetate of soda was then added, and when cold, phenylhydrazine acetate. The precipitate was similar to A. It was filtered, washed, dried, and analysed.

(*a*) o·1157 gave o·2659 CO_2 and o·0586 H_2O.

(*b*) o·1003 gave 11·7 c.c. N at 21° and 718 mm.

Hence—

Carbon	.	.	.	.	.	62·68
Hydrogen	.	.	.	.	.	5·60
Nitrogen .	.	.	.	.	.	12·7

This body appeared to be an osazone of a derivative of similar molecular dimensions to that which yielded A. The hydrolysis had only affected a partial resolution. On heating the filtrate from this osazone a second osazone was formed which was identified as glucosazone.

o·1106 gave 16·0 cc N. at 22° and 716 mm.

Calculated for glucosazone

N. 15·8   15·68

The particular interest attaching to these bodies is the evidence they afford of the complete hydrolytic break-down of the fibre substance as the major chemical effect of heart damage, and that this break-down affects not only the cellulose, but groups which yield di-carbonyl derivatives, which corresponds with the general constitutional formulæ we have adopted for the lignone constituent of jute. ['Cellulose,' p. 137 and p. 158.]

These results, as contributions to the science of the subject, are only of preliminary value. The observations require extension, more particularly in operations on sufficient quantities of material to allow of purification and fractionation of the products and derivatives.

This investigation does not go further than to indicate the scope of a fuller study of the phenomena.

We may recall a previous investigation of our own ('Chem. Soc. J.,' loc. cit.) of an exceptional specimen of 'heart-damaged' fibre, from which we obtained definitely characterised 'tannins' which yielded protocatechuic acid on fusion with alkalis. This is the only case we have observed of the transition of the keto-hexene component of the lignone complex to a benzene derivative : the conditions of the transition were, however, too complex to be reproduced in our laboratory : and in any of the processes yet studied we have not obtained more than traces of aromatic derivatives.

We may also note that ground wood or 'mechanical wood pulp' is liable to disintegration having the same general features. A recent case has been investigated by F. Barnes at the Sittingbourne Paper Mills of E. Lloyd & Co., and he established the following main points : (1) The sharply local character of the change : in one and the same sheet of pulp taken from the 4 cwt. bales there were three conditions of the ligno-cellulose conspicuously marked by external appearance (a) white : i.e. normal ; (b) grey : pulp quite friable ; (c) red-brown : pulp entirely disintegrated.

The following aggregate numbers were obtained from corresponding portions :—

	(a)	(b)	(c)
Soluble in water . . .	1·8 p.ct.	20·3	14·0
Of which ' fixed ' or non-volatile	—	15·3	12·5

There was a production of volatile acid bodies in some quantity.

The extracts from (b) and (c) showed high cupric reductivity (equivalent to dextrose = 37 p.ct.).

Furfural estimations—mean of concordant numbers :—

(a)	(b)	(c)
4·5	2·5	2·1

On the other hand the furfural (4·45 p.ct) in the water-soluble fractions (b) and (c) shewed no sensible variation from the original.

Taking a general view of these effects, the immediate chemical reactions or causes are those of hydrolysis attended both by deoxidation and oxidation of specific groups of the complex. There are no changes of ultimate or elementary composition, and the cellulose is equally affected with the lignone components.

These phenomena have their special significance in relation to industry : but they point out a line of investigation of the ligno-celluloses which is calculated not only to elucidate their peculiar labile equilibrium but to contribute to their industrial utilisation.

The direction of investigation is biological, for there appears to be sufficient evidence that the primary active cause in the above-described phenomena is the growth of micro-organisms in contact with the fibre substance   The correlative cause is the labile character of the ligno-cellulose itself as a chemical individual. The phenomena are, we may presume, related to those of animal digestion and assimilation of the ligno-cellulose complex, widely distributed as it is in the plant world. Investigations by the statistical physiological method

have certainly established its digestibility and assimilability as an aggregate effect: but little light has been thrown on the mechanism of the processes of resolution in the digestive tract.

We except from this statement results of investigation of now nearly fifty years' standing on the source of the hippuric acid of the excrements of herbivora [Untersuchungen über die Entstehung der Hippursäure im thierischen Organismus: Meissner und Sheppard, Hannover 1866] which established a genetic relationship of the benzoyl glycocoll

$$CH_2 \begin{cases} NH . CO\ C_6H_5 \\ COOH \end{cases}$$

to the lignone constituents of fodder plants. Based on this, an investigation of A. Stutzer ['Berl. Ber.,' 1875, 8,575] into the identity of the actual parent group, presumed to be of definitely aromatic constitution, led to negative results. From the 'Rohfaser' of the graminea no aromatic body could be isolated in appreciable quantity.

The problem of digestibility as an aggregate result has been a subject of repeated investigation and is accepted as fully established. It also enters into the ordinary range of agricultural food-stuffs in Germany as a constituent of positive nutritive value. This value is not only admitted for the lignocelluloses as incidental constituents of green fodder plants but for its more resistant forms as in the cereal straws, and the enveloping tissues (perisperm—husk or shell) of seeds. Thus the shell of the cocoanut is employed as a component of cattle foods in Germany and for this apparently unpromising substance a digestive value has been established equal to that of a medium-class hay. Zur Bewerthung der Kakaoschalen: C. S. Fuchs. Chem. Ztg. 34, 1245 (1910).

Attention has been drawn in this country to the problem of thus utilising ligno-cellulose waste products, by the operation of the 'Bastol' Co., who treat sawdust with aqueous sulphurous acid at high temperatures (Classen process) and obtain a partially hydrolysed product, which they employ as a constituent of cattle-foods. This practice has been publicly challenged,

the matter having indeed been dealt with by the Minister of Agriculture in the ' House ' in answer to questions arising out of prosecutions for alleged adulteration of food stuffs by ' sawdust '. (19 March, 1912).

It would be out of place to enter into controversial matters, but it is right to point out that a prejudgment on a conventional impression of ' sawdust ' as ' worthless ' and therefore an ' adulterant ' of nutritive food stuffs is mere ' prejudice ' and wholly unscientific.

This same question arises as an incidental issue in the industrial utilisation of cotton hulls or seed refuse. This waste product of the cotton industry is a mixture of seed-shell (perisperm tissues) and attached cotton fibre, the fibre which for mechanical reasons resists the ginning process. A technical problem of persistent attraction has been the economical separation of the fibre—which possesses ascertained high value as an industrial ' cellulose '—from the shell which has ascertained value as a cattle food-stuff. As a mixture, on the other hand, each is an evident prejudice to the other in the utilisation of the material in either direction.

It would be out of place to discuss this problem at length, and the more so as the matter has been very fully treated in a communication by Beadle and Stevens in the ' J. Soc. Chem. Ind.,' 28, 1015.

The importance of the matter is mainly that it presents an enormous potential supply of cellulose as raw material for such industries, e.g. papermaking, as work up fibres of short length (2·0-3·0 mm.). The production of the waste hulls in the United States alone is estimated at 1,500,000 tons per annum, equivalent to say 250,000 tons of the short fibre and a corresponding proportion of shell.

The matter is thoroughly discussed by Beadle and Stevens, and their practical experience has convinced them of the prospective utilisation of the fibre on a very large scale.

Incidentally, as premised, they were required to investigate the feeding difficulty presented by the indigestible residues of cotton fibre when the hulls themselves are utilised in cattle

foods. They found that by treatment with acids, which disintegrate the fibres with conversion of the cellulose into 'hydrocellulose,' the difficulty was in large part removed, for obvious mechanical reasons, and because the ' hydro-cellulose ' was found to be digestible and assimilable.

A further development of the industrial outlook results from the perfected mechanical separation of fibre from shell, under the patents of De Segundo, 3268 and 11,137, 1908. By these machines, which combine mechanical attrition with cyclonic air-blasts to remove and transfer the specifically voluminous fibre, the concentration of the latter reaches the high figure of 90-95 p.ct. (equivalent to 82 p.c. cellulose as purified and bleached fibre). This concentrated fibre is now produced on the large scale by the American Cotton, Hull, and Fibre Co., a company of mainly English proprietorship, owning and working the above patents.

TEXTILE BLEACHING PROCESSES.

In this important branch of chemical industry practice conserves its fundamental features unchanged, and it would be out of place to enter into the progressive perfection of details. We have to mention an investigation of an incidental issue of technical importance in all processes where chlorine or hypochlorites are used as the 'bleaching' agent, arising out of their characteristic reactions with the amino groups of the nitrogenous colloids or proteins, producing chloroamine derivatives. These reactions and their technical consequences in the textile bleaching processes will be found fully described in a communication by the authors in ' J. Soc. Chem. Ind.,' 27 (1908).

The following points which we therein established may be noted. The protein-chloroamines are the analogues of the simplest chloroamine NH_2Cl (F. Raschig, ' Berl. Ber.,' 40, 4586). These are relatively stable, and the Cl is ' active ' in the sense of the ' activity ' of hypochlorite Cl, and reacts with 2 mols.

HI — thus $X \cdot H \cdot Cl + 2HI = I_2 + HCl + XH_2$. These reactions may be employed for the quantitative estimation of ' proteins,' as e.g. of gelatin in papers.

They are conspicuous in 'flax bleaches, since nitrogenous colloids are present in notable proportion in the non-cellulose complex associated with the cellulose.

Since the chloroamines resist washing and are relatively stable, they are present in yarns and cloth, fully washed from the ordinary ' bleaching ' operation, and if dried, even after further ' souring ' or acid treatment followed by exhaustive washing, they persist and are only slowly decomposed on storage. Decomposition is attended by the production of acid, and hence the particular cause of damages to textiles, frequently observed but previously unexplained.

Since the publication of our paper we note that the investigations are generally confirmed and accepted by technologists in this field, and therefore this brief record needs no extension to emphasise the technical significance of chloroamines.

We merely mention an interesting crystalline chloroamine obtained by interaction of formaldehyde and hypochlorites as a further development of these investigations (Cross, Bevan, and Bacon, ' J. Chem. Soc.,' 97, 2404 (1910)).

PAPERMAKING INDUSTRY.

In this field we notice a contribution to the theory of sizing with rosin compounds. This universal routine operation and practice, though of secondary interest, involves factors of fundamental importance in the production of the cellulose fabric or tissue which we know as paper. In the manufacturing process it has long been recognised that colloidal hydrates, both organic (cellulose) and inorganic (alumina), play an important part. The function of resin acids in conferring water-resistant quality has been a subject of considerable controversy, with corresponding divergency in method and practice. The old

practice of using 'neutral' sizes has been largely modified in recent practice in the direction of using 'acid' sizes, containing, that is, from 20-30 p.ct. of the total rosin acids in the free or uncombined state. This modification is attributable in large part to the influence of the brochure of C. Wurster, ' Le Collage des Papiers ' ('Bull. Mulhouse,' 1878, pp. 766-801). This exposé, however, is manifestly defective in leaving out of consideration the complementary factors represented by the colloidal hydrates, viz. of cellulose and alumina, and also of the complex interactions of both with the resin compounds added to the beater ('Papermaking,' 3rd ed., p. 211, Cross and Bevan).

A critical study of these factors from a new point of experimental attack is contained in a communication of which we give an abstract.

THE SIZING OF PAPER WITH ROSIN COMPOUNDS.

J. S. REMINGTON, D. BOWACK, and P. DAVIDSON

('J. Ind. Eng. Chem.,' 1911, 3).

The present practice of papermakers is to employ a rosin size containing variable large proportions of the free rosin acids, which on dilution of the 'strong size' remain as an emulsified-suspension in the solution of the 'neutral size'.

This practice is the outcome of the investigations of C. Wurster ('Le Collage des Papiers,' 'Bull. Mulhouse,' 1878, 726), who found that on exhausting sized papers with ethereal solvents resin acids were dissolved, and who deduced from these results that free resin acids are the effective sizing agents, and that they resulted from the decomposition of neutral aluminium resinate by sulphate of alumina, always used in excess. The authors now show that the neutral alumina resinate is not decomposed by sulphate of alumina as supposed by Wurster. On the other hand, it is fractionated by treatment with ether

and with alcohol. The following results of experiments are typical :—

Aluminium Resinate	Approximately $Al_2(C_{44}H_{62}O_5)_3$	
	Found	Calculated
Al_2O_3	4·56	4·94

Fractionated by ether at ordinary temperatures, extreme variations of percentage numbers :—

Residue	Ethereal solution	Al_2O_3 p.ct. residue	Al_2O_3 p.ct. soluble solids
30·0-40·0	70·0-60·0	6·2-10·6	0·3-1·3

The extraction of papers by ether results in the removal of 60-90 p.ct. of the total resin, but there is no evidence that the resin acids so extracted are to be regarded as 'original free acid,' and no conclusion is justified that 'free resin acids' are particularly efficient in comparison with the 'original neutral resinate'.

After extracting the papers with ether, it was found that they still showed the characteristics of sized papers, and were more or less ink-resisting.

Observations on neutral alumina resinate show that when freshly precipitated, and therefore in the hydrated state, it differs in solubility and other properties from the air-dried product.

This change of properties, and indeed of composition on dehydration, is no doubt due to interior molecular change and rearrangement of the reactive group.

The authors confirm Cross and Bevan ('Papermaking,' 3rd edition) in the view that further complications of the same order result from the association of the precipitated resinate with colloidal cellulose in the actual sizing process, and that the process itself is a typical illustration of colloidal interactions of a high order of complexity, and therefore requiring much further investigation for its elucidation.

On this communication we should submit the following observations :—

On the theoretical grounds : alumina is highly colloidal and an oxide of marked amphoteric character. Alumina, therefore, in combination with resin acids (abietic acid may be formulated as $C_{18}H_{27}$. COOH, M. H. Endeman, 'J. Amer. C. S.,' 1905, 33, 523) is an equilibrium variable with the degree of associated hydration of the ' salt '.

Cellulose also represents a variable equilibrium of constituent groups similarly affected by its state of hydration.

Cellulose—alumina-abietic acid—is consequently a necessarily variable colloidal complex. This we have always considered to be the necessary basis of the phenomena and process of engine sizing.

Practically, we have shown that sizing with rosin acids, in conjunction with viscose, very much increases their efficiency.

The conditions here obtaining obviously eliminate the action of free resin acids, even when an ' acid ' size is actually used. On both theoretical and practical grounds, therefore, there are anticipations of the revelations of the present authors' experimental investigation, which fully confirm their deductions and predictions.

The phenomena of the ' beating process,' or more generally of the preparation of the paper mass, as a complex aggregate of colloidal hydrates, will be seen to involve fundamental principles, and progress from the crude empiricism which still regulates general practice lies only in the direction of intelligently applying these principles.

These results give a more comprehensive view of this long-established process, and incidentally reveal an obvious defect in the analytical method adopted by Wurster, as in the conclusions drawn from its results.

We have been particularly impressed with the doubtful efficiency of free rosin acids as sizing agents from our experience with ' viscose ' used in engine sizing. The alkalinity of viscose is such as to ensure that any ' rosin size ' used conjointly acts

in the form of 'neutral size' even if added in the 'acid' state. Notwithstanding this it is invariably found that its efficiency is very much increased by association with the colloidal cellulose hydrates resulting from the decomposition of the xanthate.

The problem of rosin sizing, therefore, is formally re-opened with experimental evidence in favour of the use of 'neutral size'. But beyond this, the above authors make out their case for a re-investigation of the process as a typical case of colloidal interactions, with resulting equilibrium of chemical factors of a high order of complexity, in which therefore a number of conditions are influential—including the 'time factor'—which are usually ignored in chemical reactions.

SPECIAL CELLULOSE INDUSTRIES.

This section we take to comprise manufactures based upon the chemical derivatives of cellulose. Actually they depend upon the conversion of cellulose into a plastic colloidal modification, usually a synthetical derivative and generally an ester. These industries, which mark the later phases of development of cellulose technology, no longer represent a narrowly specialist movement, but have attracted workers of all grades and command general attention and interest.

The most prominent of the new industries is that of the 'Artificial Silks' (lustra-cellulose), and the last five years has been a period of active evolution, marked commercially by a rapid gravitation to the level of competitive prices. This shrinkage of selling price has had the long foreseen effect of arresting the development of the collodion processes. It has necessarily accentuated the struggle between the cuprammonium and viscose processes, not merely on the question of cost of production in relation to selling prices, but on fundamental elements of textile quality which are asserting themselves as influential factors with the increasing textile uses of

these artificial fibres. There is a consequent displacement of 'cuprammonium' by 'viscose' silks.

The production of structureless cellulose in transparent sheet or film has been suggested by many of the realised applications of viscose, but the manufacture of cellulose film from viscose by continuous processes is a result attained only after long years of persistent study of the exceptionally complex technical problem.

Since the discovery of viscose it has been employed, under various conditions, in technical and industrial applications which depend upon the production of a cellulose film generally upon a surface of wood, paper, or textile fabric. The most important problem presented, however, is that of preparing the film, otherwise than on a supporting surface : further to prepare the film, necessarily by a 'continuous process,' of extreme tenuity and to retain in the finished film the characteristics of a homogeneous transparent solid. Thus the production of a film which is a very simple process as a discontinuous laboratory operation becomes a highly complex industrial problem in the presence of the exigencies of industrial production, together with cost, seeing that the film must be made in lengths of 1000 to 10,000 metres, at an average width of 1 metre and at a thickness 0·25 mm. down to 0·01 mm.

The production of a chemically pure cellulose from the xanthate further involves the following treatments in order : (1) Coagulation, (2) purification from sulphur, (3) bleaching and purification by very special washings, (4) drying. In addition to these operations the film is to be coloured, by dyeing processes, and in many cases also embossed.

A very evident complication of such processes is the continuous change of dimensions of the cellulose as it passes from a condition of precipitated hydrate to that of dehydrated cellulose : actually the shrinkage of width is 30-40 p.ct.

This complex succession of operations has been real-

ised as a continuous mechanical operation through one machine.

The film machine with its various successive sections which effect the treatments above indicated, has a length of 50-60 metres, and the evolution of this complex mechanical contrivance is due to Monsieur Brandenberger, director of the Teinturerie de Thaon, and has been patented by him, with the Soc. Anonyme, Blanchisserie et Teinturerie de Thaon (les Vosges).

It remains to be stated that a viscose answering the requirements of this highly perfected process has also been the subject of very special study, and this has been in the hands of Monsieur L. Naudin, and patented by him jointly with the Société Française de la Viscose, Paris.

The 'viscose film' (cellulose) under the powerful auspices of the Société Industrielle de Thaon is at length a *fait accompli*, and is an article of commerce under the descriptive term 'Cellophane'.[1]   The film is produced in a great variety of decorated forms which find corresponding applications.   Technically, however, these are of subordinate interest.

CELLULOSE ACETATE.

The industrial development of the acetates of cellulose has not reached large dimensions, even where cost is not the determining factor.   It is evident that the more important of such applications of the acetates would be in substitution of the nitro-celluloses as the basis of 'celluloid' or 'xylonite' manufacture, products which with their extraordinary qualities as structural solids, unite certain defects of inflammability and instability. Celluloid and xylonite have taken a large and always expanding position in industry, notwithstanding these secondary defects, but in certain cases, as for instance in the application of

[1] Specimens of " Cellophane " film will be found in the pocket attached to the binding cover.

the celluloid film to lantern projections, the consequent risks are such that the cost of film material has no direct relation to the values involved. Hence the several centres of production of these compounds have been actively engaged in perfecting an acetate film fulfilling the requirements of the cinematograph; some of these films are 'on the market'. It has been found that the properties of the pure acetates are not such as to adapt themselves to all the exigencies of such films, and by way of correcting certain defects various admixtures are employed.

The general aim of investigators in this field appears to be defined by the accepted principles of celluloid manufacture, and we may direct attention to the special features of this manufacture, from a point of view which does not appear to have been systematically treated. In the following brief exposé we have drawn upon the special knowledge and experience of our friend Dr. J. N. Goldsmith, who directly contributes the matter.

The central technical point in this manufacture is the function of camphor in the nitro-cellulose 'composition' which constitutes celluloid. (As a matter of observation the action of camphor is to determine interior modifications (structural) of the cellulose ester colloid.) It not only confers a true and remarkable plasticity upon the mass, but the effects are permanent.

Separating this effect, the action of the liquid solvents which are used in association with camphor, is of quite secondary importance.

These liquid solvents, used as diluents, are usually alcohols, ketones or carboxylic esters, and joint solvents of the camphor and cellulose nitrates.

Hydrocarbons or their chlorinated derivatives cannot be employed as solvents.

The important distinction of 'celluloid' from the acetate

colloids however prepared, is in respect of plasticity of the finished product, the lack of which is the chief industrial defect of the latter.

This defect is no doubt referable to constitution in the chemical sense, and influenced by the relation of chemical function of the cellulose acetate, to the solvent used which is generally a chlorinated hydrocarbon.

The nature of the celluloid colloids has not yet been investigated by the methods of modern colloidal chemistry, but an explanation of the phenomena attending its production may be attempted on the following lines :—

The solid nitro-cellulose absorbs camphor from the liquid phase, alcohol and camphor, and the colloid thus formed is at first a mass of ' gel ' cells enclosing the solution of disperse colloid in alcohol and camphor.

The milling operation causes these cells to rupture and the liquid solvent evaporates ; the viscosity of the mass increases enormously owing to the production of new colloidal surfaces. Although the concentration of the liquid phase has now altered greatly, there is, in the case of celluloid, no separation of suspensoid, or solid phase.   The nitro-cellulose-camphor-alcohol colloid is stable, independently of the incidental evaporation, of the dispersing medium, i.e. the alcohol.   When we pass from camphor to *camphor substitutes*, as the tertium quid of the celluloid in the ' dough ' stage, this independence of concentration is not exhibited by all ' pseudo-celluloids,' that is by all the complexes made up of nitro-cellulose and camphor substitute, with alcohol or other diluent.

In a number of such cases there is a separation of suspensoid, or solid phase, as the liquid solvent concentrates during the manufacture.   The possible number of liquid colloidal surfaces is thus reduced, and an aggregate with weak tensile properties results, consisting of mainly suspensoid, in weak mechanical union with gel, which may have lost its original

transparency, and exhibit a translucent milky appearance, or may even be white and completely opaque.

In these extreme cases, the articles manufactured are hard, non-plastic, and very brittle ; cases however are known in which the production of a somewhat brittle non-plastic colloid is *not* associated with loss of transparency.

The majority of the camphor substitutes, however, suffer from defects of another kind. The resulting colloidal aggregate has the desired plastic qualities, when heated, but as regards rigidity and elasticity in the cold, it is more or less deficient.

The colloid at ordinary temperatures, exhibits the properties of the slightly warm camphor celluloid.

A consideration of the constitutional characteristics of these camphor substitutes shows that they are benzene or hydro-benzene derivatives or analogues, containing carbonyl, carboxyl-ethyl, acetylamido benzoyl-amido, and sulphoxyl-amido groups, etc.

A certain resemblance to camphor may be traced in the presence of a ketone group, methyl groups in some cases, and of the hydroaromatic or aromatic nucleus, the degree of re-semblance or constitutional analogy being generally related to degree of efficiency. The physical properties of these camphor substitutes are, however, unfavourable, compared with camphor ; their melting-points usually lying about $50°$ nearer to the atmospheric temperature.

This fact is probably connected with the want of rigidity and elasticity, in the camphor substitute aggregate.

The plasticity of camphor celluloid at about $80°C.$ is due to the formation by fusion, of liquid phase, lowering the internal friction between the colloid surfaces, of the gel. The valuable rigidity and elasticity of camphor celluloid at ordinary temperatures, may be due to the more or less complete absence of liquid phase.

Proceeding to the consideration of the camphor-substitute-

cellulose-acetate aggregate; it appears that the gel in this case is not so independent of the concentration of the dispersing solvent. Camphor itself with cellulose acetate does not yield a satisfactory product. At first sight there would appear to be a far larger number of camphor substitutes available for colloid-ising cellulose acetate, owing to its exceptionally non-reactive character as compared with the reactivity of cellulose nitrates.

Thus for instance in regard to the nitric esters, camphor substitutes containing the $NH\,CH_3$ group in an aromatic nucleus will rapidly react with the nitrocelluloses to form nitrosyl compounds, when the celluloid containing these 'substitutes' is heated. As regards the acetic esters, in spite of the fact that so many compounds are apparently available as colloidisers, and of the probability of one or other developing special colloidal characteristics we observe a general and characteristic inferiority: and indeed there appears to be lacking in cellulose acetate the structural property peculiar to the nitro-celluloses, which may be due to retention of the characteristic configuration of cellu-lose or may be conferred possibly by the oxygen atoms of the NO_3 groups in cellulose nitrate.

In accordance with this hypothesis it is to be noted that the various cellulose acetates are not derivatives of the same cellu-lose complex which is contained in the nitric acid esters.

It is a matter of fact, whatever the constitutional cause, that the whole range of the known cellulose acetates, chloroform-soluble, acetone-soluble, or alcohol-soluble, and of widely vary-ing viscosities, do not produce a celluloid-like mass with cam-phor substitutes which possess the technically valuable qualities of ordinary celluloid.

Notwithstanding its structural inferiority as the basis of films and massive articles, the production of these is being developed industrially at various centres—chiefly in Germany and America.

In addition to the above applications the technical applica-

tions of cellulose acetate in electrical industry deserve special mention. This branch is being developed from an active centre in Boston, Mass., under the patents of Mork for special conditions of manufacture of the acetate ('normal fibrous cellulose acetate,' U.S. patent 854,374, 1907) and for special solvents ('methyl formiate as a solvent for celluiose acetate,' U.S. patent 972,464, 1910).

The following short paper on wire insulation appears in the 'Engineering News' 1908, 54-59, and deals with the fundamental technical factors :—

CELLULOSE ACETATE AS WIRE INSULATION.
R. FLEMING.

(From the 'Engineering News,' Jan. 16, 1908).

Insulated copper wire is a ruling factor in the design and manufacture of electrical apparatus, and any process which reduces the cost of the insulated wire or raises its value is of great industrial importance.

Silk and cotton are the materials which have been mainly used for insulating purposes. The former is relatively expensive, while the latter, though cheap, occupies an unfortunately large proportion of the winding space, especially in the case of fine wires. Various colloidal solutions have been applied to wires in the attempt to secure a thin, permanent insulation, which would be more economical to use than silk or cotton. Cellulose acetate, enamel, collodion, casein, albumen, glue, rubber, and silk solutions, have been tried with more or less favourable results ; of these cellulose acetate and enamel have proved to be best adapted to the requirements.

The mechanical properties of the cellulose-acetate film give it special advantages in insulating very fine wires. Its elasticity permits of considerable stretching of the wire before rupture takes places, thus ensuring continuous insulation between

wires on the finished coil.   Its specific resistance is very high, so that the film even though thin, provides ample insulation between turns and between the layers of superposed wire.   The evenness of the coating, and the regularity with which the film can be applied to the wire, are important advantages ; the finished wire is free from imperfections of coating, and presents an attractive appearance.   This insulation can be coloured to any desired shade to harmonize with the surroundings.   In case of very fine wire, a bright green makes a satisfactory colour, rendering it easy for the operators to see the wire, and to detect irregularity in the winding ; but if these fine wires are coloured a neutral tint, they are practically invisible and winding them is a difficult operation.

The sizes of wire best suited to this process are from 0·003 in. in diameter, or even finer, to those of 0·005 in.   These diameters correspond to about 40 and 35 B. & S. gage.   For larger sizes, the enamel coatings are more suitable.

Cellulose acetate has been used for a number of years for the windings of meter armatures, where light weight is of great importance.   Table I shows some of the more important comparisons of data :—

TABLE I.—COMPARISON OF CELLULOSE ACETATE, SILK AND COTTON INSULATION.

·003 Diameter of Copper		Acetate	Single Silk	Single Cotton
Thickness of insulating film	.	·0005	·0009	·00175
Wire space factor . . .		·442	·313	·167
Weight per thousand feet (lbs.) .		·033	·036	·049

With acetate-coated wire the greatly improved space factor means, that for a given number of turns on a given form, the mean length of turn and total weight of wire is greatly reduced.   This is shown in Table II, which is drawn up on the basis of a perfect winding :—

TABLE II.—Comparison of Coils Wound with Wires Insulated with Cellulose Acetate, Silk and Cotton

Diameter of spool 1 in.   Number of turns 100,000
Length of spool 1 in.   Diameter of copper ·003 in.

Insulation of Conductor	Outside Diam. of Coil (in.)	Resistance (Ohms)	Weight of Coil (lb.)	Price per lb. to give same cost of Coil
Acetate	4·20	71,300	2·22	$ 7·50
Single silk . . .	5·53	89,500	3·04	5·50
Single cotton . . .	9·50	144,000	6·73	2·50

The great decrease in size shown would, in itself, often be enough to warrant the use of acetate wire.

Another great advantage of acetate wire is that it is not affected by ordinary atmospheric conditions. Complete drying and impregnating processes are necessary for fibrous insulations, if long life is to be expected of them. Manufacturers of telephones and other specialities, who use fine wires, will find film-coated wires of very great service in reducing the cost, and also the size, of their apparatus.

In the Lynn acetate wire-coating machines the solution automatically passes from the mixing reservoirs to the coating portion of the apparatus. Here, by a system of transfer wheels, the solution is applied to the revolving coating roll, which, in turn, deposits it on the moving wire. The quantity of solution placed on the wire must be closely adjusted, therefore mechanical scrapers are employed, which remove the excess and leave just the proper amount to be deposited.

After receiving its coating of solution, the wire passes through the oven at the rate of several hundred feet per minute. The volatile solvent is here driven off and the coating hardened, after which the process is repeated until numerous coatings have been applied. This method ensures an even distribution of the film over the whole surface of the wire. To keep the

fine wire moving at such a high rate of speed a very delicate adjustment of the moving parts is required, for the slightest unevenness of motion is sure to break the wire.　This is prevented by friction drives and friction tension·devices, which ensure a uniform motion.

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